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SUPPLEMENT TO MELLOR'S
COMPREHENSIVE TREATISE ON
INORGANIC AND THEORETICAL CHEMISTRY

VOLUME VIII
SUPPLEMENT III

# SUPPLEMENT TO MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

## VOLUME VIII

## SUPPLEMENT III

## P

# A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

By J. W. Mellor, D.Sc., F.R.S.

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Supplement to

MELLOR'S COMPREHENSIVE
TREATISE ON

# INORGANIC AND THEORETICAL CHEMISTRY

*Prepared under the direction*
*of an Editorial Board*

## VOLUME VIII

## SUPPLEMENT III

## *Phosphorus*

LONGMAN

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# PREFACE

This Supplement has been prepared following the general editorial policies already outlined in the Prefaces to Volume II, Supplement I (originally called Supplement II, Part I) and Volume VII, Supplement II. However, in certain respects this Supplement differs from previous volumes of the series; it represents a serious effort to tailor the 'Mellor' treatment to the prevailing balance of importance of the different areas of chemistry treated, and to aspects of special interest in the chemical industry. This volume therefore gives prominence, on the fundamental side, to the extremely interesting structural chemistry of phosphorus compounds, the diversity of compounds of phosphorus and nitrogen, and organophosphorus chemistry. Section XXXIII, on organic derivatives of phosphorus, is in fact a monograph providing, with almost 2500 literature references, a unique key to organic compounds of which phosphorus is an important constituent; it is a definite but useful break from the early traditions of 'Mellor'. The thorough treatment of metal phosphides as a group is also of special interest, because these interesting substances are so often covered in reference literature by scattered sections linked with the metals they contain.

A further new feature in this Supplement is the participation of a specialist Editor to give general guidance and supervision to the general arrangement of the volume, selection of contributors, and preparation of manuscripts. Dr A. F. Childs, Research Director of Albright & Wilson Ltd (Oldbury Division) has given extremely valuable help to the Editorial Board in this capacity, and the whole volume reflects the close acquaintance with phosphorus chemistry shown by Dr Childs and members of his staff. The Editors and Publishers also gratefully recognize the extensive help given by Miss M. J. Moore, formerly Secretary to Dr Childs, in preparing and checking the typescript of this Supplement.

Much of the initial editorial work on this Supplement was done by the senior member of the Editorial Board, Mr A. A. Eldridge, who died in 1970 after a long and fruitful period of work on 'Mellor'. Mr Eldridge was one of the small team of chemists which developed, after the Second World War, the general plan for supplementation of the original 'Mellor Treatise', and he retained a very active part in editorial planning, revision of manuscripts, and proof correction until a few weeks before his death. His thorough appreciation of the requirements of a reference work on inorganic chemistry, and the high standard set by his editorial work, have been sadly missed by the other editors in completing the present volume.

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# ABBREVIATIONS

| | |
|---|---|
| absolute | abs. |
| alternating current | a.c. |
| ampère-s | amp. |
| Angstrom unit-s | A. |
| atmosphere-s (after a numeral) | atm. |
| atomic weight | at. wt. |
| boiling point | b.p. |
| British thermal unit-s | B.Th.U. |
| Calorie-s (large) | kcal. |
| calorie-s (small) | g.-cal. |
| centimetre-s | cm. |
| cubic centimetre-s | c.c. |
| density (with a numeral) | $\rho$, *d* |
| direct current | d.c. |
| electromotive force | e.m.f. |
| foot, feet | ft. |
| freezing point | f.p. |
| gram-s (with a numeral) | g. |
| hour-s (with a numeral) | hr. |
| inch-es | in. |
| kilogram-s | kg. |
| kilowatt-s | kw. |
| litre-s (with a numeral) | l. |
| melting point | m.p. |
| milliampère-s | ma. |
| millilitre-s | ml. |
| millivolt-s | mv. |
| minute-s | min. |
| molecular weight | mol. wt. |
| parts per million | p.p.m. |
| potential difference | p.d. |
| second-s (time only) | sec. |
| specific gravity | sp. gr. |
| square centimetre-s | sq. cm. |
| vapour density | v.d. |
| vapour pressure | v.p. |
| volt-s | v. |
| watt-s | w. |
| wave-length | $\lambda$ |

Abbreviations of Journal titles, etc., in references are listed in Volume VIII, Supplement 1, Nitrogen (Part I), pp. xi–lxviii. A few additional abbreviations have unavoidably been introduced; these conform to current practice in 'Chemical Abstracts'.

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# PHOSPHORUS

## SECTION I

## THE HISTORY AND OCCURRENCE OF PHOSPHORUS

BY D. R. PECK

DURING the past thirty years the distribution and composition of phosphate deposits have been studied extensively, particularly with reference to ores of commercial value. Geological explorations of the earth's crust, together with an examination of meteorites, have enabled estimates to be made of the abundance of phosphorus in the universe. F. W. Clarke and H. S. Washington (Mellor, VIII, 732) calculated the average composition of rocks from the results obtained by analyzing many rocks and minerals. The method used in this calculation has been said[1] to give high results for phosphorus pentoxide. After revision of the earlier data and calculations, it was estimated that the average percentages of phosphorus in igneous and sedimentary rocks were 0·075–0·080 and 0·072, respectively. The analysis of meteorites[2] indicates that these contain about 0·2% by weight of phosphorus. The more recent values[3] for the distribution of phosphorus have been summarized by Van Wazer[4] as shown in Table 1.

*Table I.—The Abundance of Phosphorus*

| Source | Wt.-% of P |
|---|---|
| Meteorites—metal phase | 0·22 |
| Meteorites—sulphide phase | 0·31 |
| Meteorites—silicate phase | 0·0145–0·0170 |
| Gross abundance in meteorites | 0·18–0·19 |
| Igneous rocks | 0·07–0·13 |
| Sandstones | 0·04 |
| Red clay | 0·14 |
| Shales | 0·08 |
| Limestones | 0·02 |
| Gross abundance on earth's surface | 0·10–0·12 |

From the above data phosphorus is eleventh in the order of abundance of the elements in the igneous rocks of the earth's crust, thirteenth in meteorites and twenty-fourth in the sun's atmosphere. Van Wazer computed the amount of phosphorus in the earth to be $10^{25}$ grams or $10^{19}$ tons, and estimated that the abundance in the universe was about the same as the gross abundance in the earth's crust (Table I).

Phosphorus differs from carbon, hydrogen, oxygen, nitrogen and sulphur, the other major non-metallic elements in the animal and vegetable kingdoms, in not being present in the earth's atmosphere. It is, however, found in traces in lakes, rivers and oceans. In sea water the concentration of dissolved phosphorus is very low at the surface. This increases to a maximum value of 0·04–0·10 p.p.m. at a depth of about 800 metres, and thereafter remains almost constant at this value down to the sea bottom.[5] According to Van Wazer[4] the total amount of phosphorus dissolved in the seas is about $10^{17}$ grams.

## GENESIS AND FORMATION OF PHOSPHATE ORES

### IGNEOUS ROCKS

The geology and mineralogy of phosphate deposits indicate that all the phosphorus was present originally in igneous rocks. Phosphate is found, even if only to the extent of about 0·1%, in almost all present-day igneous rocks, where it usually occurs as apatite. The latter is most often in the form of minute crystals in gneiss, granite and diabase, and nearly all the recognized species of phosphates are to be found in the pegmatites or coarsely crystallized granites. It has been estimated that at least 95% of the phosphorus content of igneous rocks is present in the form of apatite.[6]

### SEDIMENTARY DEPOSITS

In the course of geological time the igneous apatites became transformed into phosphorites of marine origin, the second main type of phosphate deposit. Joly[7] put forward a theory of periodic revolutions to account for the changes in the earth's crust known to have occurred in the geological history of the world. There is evidence to show that frequent catastrophic events, such as extensive earthquakes, volcanic eruptions and huge tidal waves, have occurred during periods when the earth's surface was unstable. These phenomena could have caused the igneous apatites to disintegrate, and subsequent leaching of the rocks by water would result in large quantities of phosphate being carried into the seas, where it was subject to biological utilization. Eventually the greater part of this leached phosphate was again deposited as sedimentary formations, usually as pellets a few millimetres in diameter. In some areas, such as the Western United States[8] and the Kara-Tau region of the U.S.S.R.,[9] this type of deposit occurs in layers, probably as the result of geological action causing compression followed by lifting.

The part played by sea water in the formation of sedimentary phosphate deposits has been discussed by a number of authors.[10, 424] Kazakov[11] reviewed and discussed the earlier theories of the origin of phosphates[12] in the world and considered that many of the deposits were of marine origin. They were formed by chemical precipitation of the phosphoric acid present in sea water. Ocean currents carried the phosphate, which was in solution in the open sea, to regions where calcium carbonate predominated and thus caused precipitation of calcium phosphate.[13] Phosphorite deposits were therefore formed on or near Continental shelves. Kazakov described the temperature conditions and the chemical composition of sea water necessary for the formation of phosphorites, in relation to their basicity and the variation in their content of fluoride and phosphate ions. Equilibria in the $CaO–P_2O_5–H_2O$ and $CaO–P_2O_5–HF–H_2O$ systems at low ion concentration were investigated in order to determine the physicochemical conditions relating to phosphate deposition.[14] However, the results of this work did not entirely prove the theory put forward, mainly because the concentrations of CaO, $P_2O_5$ and F, corresponding to the solid phases in the systems studied, differed from the concentrations of fluorapatite and hydroxyapatite found in sea water. Further, the presence of carbonate and other salts in sea water was not taken into consideration. On the other hand, chemical analysis and geological examination of phosphorite deposits supported the hypothesis. More recent studies[15] in which the systems were examined in the presence of 3·5% sodium chloride showed that the CaO content in Kazakov's data was much too low to correspond with that in sea water. In the $CaO–P_2O_5–NaCl–CO_2–H_2O$ system the phosphorus content of the saturated solutions increased with the carbonate ion concentration. This may be a factor in the enrichment of phosphates in marsh waters containing carbonate.

In an alternative hypothesis[16] it is considered that calcium carbonate becomes phosphated on the sea-bed. Nodules of calcium carbonate are formed from the remains of plant and animal life and shells deposited in the sea, by the movement of currents along the ocean floor. Sea water at depths of more than a few hundred metres is thought to be saturated with apatite,[17] so that stationary or slow moving particles of calcium carbonate can become phosphatized slowly by a process of exchange with the saturated apatite solution. Oceanographic expeditions show that phosphate concretions are forming around the remains of fish lying in the ooze on the bottom of deep seas. Phosphate deposits may therefore have formed simultaneously with the laying down of the strata in which they occur.

In some land areas, particularly where wind, temperature and moisture conditions were suitable, extensive weathering of rocks occurred. Some limestone and dolomite rocks of marine origin in these regions contained apatite, and in the process of weathering, the calcium carbonate was slowly dissolved away, leaving a higher grade phosphate deposit behind.[18] Near river areas, boulders, nodules and pebbles of this enriched phosphate were carried from the original site and subsequently deposited on the river bottom.[19, 20] Such deposits are generally small, occur in patches and usually have a low phosphorus content.

### EFFECT OF VEGETATION

A third type of phosphate deposit has been formed by a phosphating process similar to that described above. Water in contact with decaying vegetation may become sufficiently acidic to dissolve phosphate from sedimentary rocks. This is carried in solution and subsequently reprecipitated on suitable rock formations to give rise to a phosphatized rock. Exposure of guano deposits to rain removes their soluble constituents, and the dissolved phosphate may become fixed by reaction with the underlying rock. In this way the coral limestone of the Ocean Islands has been phosphatized. A similar reaction occurs with igneous rocks such as basalt, but these are a less important source of phosphorus because of the presence of iron and aluminium in the original rock. These leached guanos and phosphatized limestones are sometimes known as sombrerite.

### GUANO

Guano is the fourth principal type of phosphate. In coastal areas such as those of Peru and Chile and on some islands, e.g. the Seychelles and Ocean Islands, bats and sea-fowl have nested for long periods of time. The excreta of these, together with such remains as bones and feathers, have given rise to the material known as guano. The main constituents of this are nitrogenous substances such as guanine and uric acid, calcium phosphate, and potassium and ammonium salts.

Igneous rocks in general are not important as a commercial source of phosphorus because of their low phosphate content. Exceptions to this are the igneous phosphate deposits of the Kola peninsula in the U.S.S.R. and those found in Uganda and eastern Transvaal regions of Africa. The main sources of phosphates at the present time are the sedimentary deposits. They occur in rock formations of all ages as far back as the Cambrian period (about 500 million years ago). Guano deposits are of value more as fertilizers rather than as a raw material for production of elemental phosphorus or phosphoric acid. At present they account for between 5 and 10% of world phosphate production, but in some areas the deposits have been depleted.

## DISTRIBUTION, NATURE AND COMPOSITION OF PHOSPHATE DEPOSITS

Deposits of phosphate have been found in many countries, but not all of the ores are suitable as a commercial source of phosphorus. New deposits are still being revealed by geological surveys and prospecting. It is apparent that in Africa, Asia and South America large areas where phosphates are likely to be found have still to be searched. Estimates of the reserves of phosphates in the world have been made from time to time, but these depend on what is meant by a reserve. Some deposits, for example, are isolated or too small and patchy to be of value. Many low grade ores, some marine phosphorites, and material which could be recovered from phosphate-containing iron ores cannot at present be utilized economically. Some of these types of deposit may well be larger than those of the higher grade phosphates now being mined. For example, it has been estimated that in the Western United States the low grade ores may amount to $10^{11}$ tons.[21] Taking these factors into account, Van Wazer[4] states that the world reserves of phosphate which can be mined economically are probably $3 \times 10^{16}$ grams ($3 \times 10^{10}$ tons). He gave estimates, compiled from various sources of information,[21-3] of the maximum reserves which could be mined in various countries. A summary of these is shown in Table II.

*Table II.—World Deposits of Phosphates*

| Location | Maximum deposit (million tons) |
|---|---|
| Morocco | >21,000 |
| Tunisia | 2,000 |
| Algeria | 1,000 |
| Egypt | 180 |
| U.S.A. | 13,500 |
| Brazil | 570 |
| Mexico | 215 |
| U.S.S.R. | 7,600 |
| Europe | 440 |
| Australia, Nauru and Ocean Islands | 180 |
| Christmas Island | 50 |
| Indo-China | 18 |
| India | 10 |
| Israel, Jordan | 4 |
| China | 3 |

The higher grade deposits, containing 20% $P_2O_5$ or more, are mostly found in the United States, the Kola peninsula of the U.S.S.R., North Africa and the Nauru and Ocean Islands in the Pacific. Typical percentages[22, 24, 114] of the major constituents of the highest grade ores from these regions are shown in Table III.

*Table III.—Composition of High Grade Phosphate Ores*

| | Florida | Tennessee | Morocco | Tunisia | U.S.S.R. | Pacific |
|---|---|---|---|---|---|---|
| $P_2O_5$ | 35·2 | 34·2 | 35·0 | 27·8 | 40·3 | 39·2 |
| $CaO$ | 49·2 | 49·0 | 53·0 | 46·0 | 52·3 | 53·8 |
| $Al_2O_3$ | 1·0 | 1·2 | 0·3 | 1·8 | — | 0·2 |
| $Fe_2O_3$ | 0·8 | 2·3 | — | 0·5 | 0·5 | — |
| $SiO_2$ | 5·0 | 5·3 | 0·4 | 8·0 | 0·4 | 0·2 |
| $SO_3$ | 1·2 | 0·7 | 1·3 | 3·0 | — | — |
| $CO_2$ | 2·0 | 1·8 | 4·2 | 6·0 | — | 1·2 |
| $F$ | 3·8 | 3·5 | 4·1 | 3·5 | 3·7 | 3·0 |
| $H_2O$ | 1·8 | 1·2 | 1·2 | 2·4 | 0·7 | 2·3 |

### AMERICAN DEPOSITS

From an examination of their structural characteristics, using microscopic and *X*-ray diffraction techniques, it has been shown that many of the American deposits are submicro-crystalline fluorapatite.[25-6] In some of the ores the fluorine content is greater than that corresponding to the fluorapatite composition $3Ca_3(PO_4)_2,CaF_2$, and it has been suggested[27-8] that this could be due to the presence in them of a fluorophosphate, in which a fluorine replaces an oxygen atom in the phosphate ion.

In Florida there are two main types of rock phosphate.[22, 24, 29] One of these, known as pebble phosphate, covers an area of some 600 or 700 square miles to the east and south-east of the city of Tampa. The rock formation in this region is composed of a number of strata. As far as phosphorus is concerned the lowest stratum lies at a depth of about 250 ft. and consists of limestone overlaid with clay. This is a phosphate-bearing layer which was formed about 20 million years ago. On top of this there is a 20 ft. bed comprising a mixture of sand, clay and phosphate rock and pellets. About 5 million years ago these two strata were subjected to erosion and weathering by sea water, giving rise to a third layer containing sand, clay, and calcium and aluminium phosphates. Surmounting this is an overburden, about 20 ft. thick, of sand and quartz. As a result of weathering some of the calcium phosphate reacted with the surrounding clay to form aluminium phosphate.

Some 60 miles to the north of Tampa a second type of deposit, the hard-rock phosphate, is found. This extends northwards for about 120 miles and consists mainly of whitish boulders. The deposits are underneath a layer of sand and clay and vary in thickness from about 5 to 90 ft.

Phosphate rock has been mined since 1868 in South Carolina, mainly in the coastal region near Charleston and Beaufort. The phosphate occurs in lumps of varying size, usually covered by alluvial sands and clays. The beds contain phosphatized fossils, some 50 or 60 million years old, and fragments of vertebrata such as mastodon, horse and elephant, of the more recent Pleistocene period. South Carolina was the principal mining area until the Florida deposits were first worked in 1883. Smaller deposits have also been mined in North Carolina, Pennsylvania, Alabama and Arkansas.

The phosphate deposits of Tennessee, which are derived from limestones about 370 million years old, are small compared with those of Florida. They were formed by deposition from shallow seas and the ore occurs in the form of blue, brown and white rock. The last is heavy and massive, while the blue rock consists of phosphate pellets embedded in calcium carbonate. These two types are of less commercial importance than the brown rock which is composed of carbonate–apatite mixed with sand and clay.

The largest deposits of phosphates in the United States occur in the Western fields, covering parts of the states of Utah, Idaho, Wyoming and Montana. Although the area extends to some 100,000 square miles and is perhaps the biggest potential source of phosphates in the world (Van Wazer, loc. cit., page 980), the ores, because of their relatively unfavourable location, have only recently been worked to any extent. The deposits are known as the Phosphoria formation and originated in the Permian period about 200 million years ago. The phosphate is chiefly a carbonate–fluorapatite[30] and occurs as dense nodules, mudstones and soft shales. It may contain as much as 5% of organic carbon. The conditions of deposition were similar to those postulated by Kazakov.[13] The beds have a maximum thickness of 73 ft.[31] and are compressed and folded, particularly in the western part of the region where the rock structure is complex. A general petrographic study and classification of 21 Western phosphate ores has been made[421] and the resources of the area have been reviewed.[422]

Phosphorite deposits containing 14–21% $P_2O_5$ have been found in Mexico[32] and Texas,[33] and in California phosphate pellets containing up to 33% $P_2O_5$ occur.[34] These deposits, however, are small. Examination of the marine phosphates off the coasts of these areas showed that the minerals were chemically fluorapatite.[35] On the sea-bed off Southern California most of the phosphates are of igneous and volcanic origin[36] with about one-third as sedimentary rocks. The latter were formed mainly by direct precipitation *in situ*.[37] The rock formations in these regions date from about 170 million years ago, the most abundant being those of the Miocene period.[38]

Apatite, phosphorite, guano and aluminium phosphate deposits of commercial value occur in Brazil. In the southern area, mainly in the state of Minas Gerais, it is estimated that there are about 100 million tons of apatite containing 12–22% or more of phosphorus pentoxide,[39] and new deposits are still being discovered.[423] What may be the world's largest deposit of phosphate, containing 31·8% $P_2O_5$, has been reported from Peru.[40]

### NORTH AFRICAN DEPOSITS

The Moroccan phosphates occur to the west of the Atlas mountains, mining being centred on Khouribga about 75 miles to the south-east of Casablanca.[41] In Algeria phosphorite is found to the east of the Atlas range, mainly near Tocqueville and Tébessa. These deposits extend to the Tunisian border in the region of Jebel Kouif and thence to the area of the Tunisian ores at Gafsa. Most of these ores belong to the Lower Eocene period, about 75 million years ago. Egypt has deposits east of Keneh and in the Dakla oasis in the Libyan desert.

Major reserves of phosphate occur in Turkey. The deposits, estimated to contain at least 200 million tons of carbonate fluorapatite, are found to the south of the Anti Taurus mountains in a belt 500 km. long by 100 km. wide.[430-1]

### U.S.S.R. DEPOSITS

Phosphate deposits in the U.S.S.R. have been surveyed and examined systematically since the year 1910. The location of those known up to 1922 was mapped by Samoilov.[42] About 65% of the ores contain less than 20% $P_2O_5$ and in the remainder the maximum content is usually about 35%. In the White Sea area, however, there are on the Kola peninsula phosphates of igneous origin which contain as much as 41% $P_2O_5$. The age of these deposits, as determined by the radioactive lead method, was found to be 312–400 million years. By the argon and helium methods the figure found was 230–400 million years.[43] The mineralization of igneous phosphates of the Mtavari series has been discussed.[425] Further south near Grodno on the Polish border[44] and in the region of Podolia[45] the phosphates are mainly of sedimentary origin and contain about 20–25% $P_2O_5$. In the area of the Horyn river on the borders of the Ukraine the deposits are mostly apatite, dating from about 350 million years ago. The phosphate content is about 32% $P_2O_5$.[46]

The Moscow Basin contains phosphorites of various kinds, mostly with a $P_2O_5$ content of 10–25%.[47] Some of these originate from rocks 100–150 million years old.[48] Others are of more recent origin, resulting from sea-bottom deposits and sediments.[49] Interaction of phosphorite sands with iron-containing glacial deposits such as moraines and pyritic clays formed a mineral very similar to delvauxite, $Fe_2O_3,P_2O_5,nH_2O$.[50]

Black phosphorite nodules having the composition $2Ca_3(PO_4)_2,CaF_2,CaCO_3$ were discovered near Kursk, some 300 miles south of Moscow, and were later found in the Ukraine.[51] Petrographic examination of the phosphorites of Western Russia supported the existence of a new mineral, which was named *kurskite*, and which was shown to be distinct from *staffelite*, $3Ca_3(PO_4)_2,CaF_2,CaCO_3$.[52] Phosphate deposits in the Moscow region were said to be mainly kurskite.[49] It is possible, however, that these may have been confused with *francolite*. The separation of phosphorites into kurskite and staffelite has been criticized[53] because $X$-ray examination does not support this. Both minerals were shown to have the fluorapatite lattice and the lattice structure was not changed on removal of the carbon dioxide by heating the phosphorites to a high temperature.

Near Kursk, and extending along the basin of the Seim river to Rylsk on the border of the Ukraine, phosphorites containing 13–37% $P_2O_5$ are found. These were formed 50–100 million years ago by precipitation of the phosphate in a shallow sea, and consist mostly of quartz sandstones cemented together with the phosphate. Similar deposits occur about 300 miles to the east of Kursk in the valley of the Khoper river, and extend north-east towards Ribkin in the province of Penza. They resulted from the leaching of phosphorus-containing limestones of the Cretaceous period. The phosphorite is mixed with clay, mica and glauconite, a potassium iron silicate derived from Secondary and Tertiary rock formations.[54-5] In the Ukraine sedimentary deposits occur as a clay pebble phosphate containing 22–27% $P_2O_5$ and as sandy pebbles with a $P_2O_5$ content of 15–18%.[56] Phosphorite nodules are present in the glauconitic marl and in ammonites found in the Daghestan area of the Caucasus. These average about 21% $P_2O_5$.[57] One of the largest of the phosphorite deposits of the U.S.S.R. occurs in the region between the Vyatka and Kama rivers, 500–600 miles east of Moscow. This also is of glauconitic origin and contains about 25% $P_2O_5$.[58] South of this area, on the western slopes of the Ural mountains, there are phosphorites of limestone and dolomite origin. These are located near Sterlitamak and in the valley of the Seleuk river, about 120 miles west of Magnitogorsk.[59] The $P_2O_5$ content ranges between 15 and 34%,[60] but is mostly around 20%. The rock formation usually consists of alternate strata of grey and brown phosphorite and limestone or calcite. Weathering has resulted in the phosphate being preserved only in spots or in lenses. In the thinner strata the phosphate is amorphous or fine-grained and is mixed with carbonates, iron oxides and quartz grains.[61] The phosphorites along the Seleuk river are less stratified and often consist of a grey or black phosphate embedded in dolomite. The black variety contains as much as 31% $P_2O_5$. It is thought that they were formed by chemical precipitation from sea water.[62] On the eastern slopes of the Urals phosphorites occur in the gorge of the river Tech. They are sedimentary in nature, often consisting of layers of glauconite cemented together by calcium phosphate. The $P_2O_5$ content is about 20%. Some sediments also consist of a white, finely-grained layer of phosphorite deposited on quartz sand and feldspar, the phosphate portion containing up to 37% $P_2O_5$.[63] The phosphates of the Urals are not of great industrial importance mainly because of the depth of the deposits, their scattered distribution or the thinness of the phosphorite bed. They are, however, of some interest because they occur at the boundary of two sea sediments, which may indicate much larger deposits in the region.

Large quantities of phosphorites occur in South Kazakhstan, mainly in the Kara-Tau mountain area, approximately 350 miles north of Afghanistan.[64, 426] The deposits have been estimated to be some 315 million tons, yielding 25 tons of ore per square mile.[65] The average $P_2O_5$ content is 28%, but in some beds it is as high as 36%.[66]

In Northern Bessarabia near the Ukraine phosphorites are found in the valley of the Dniester river. They are mostly apatites and contain 36% $P_2O_5$ corresponding to 80% $Ca_3(PO_4)_2$. Geological examination indicates that they are derived from rocks about 250 million years old and their petrographic characteristics show that they are lake deposits.[67]

Polish phosphorites contain 15–22% $P_2O_5$ and occur mostly on the borders of White Russia as far north as Raków near Lithuania.[68] In middle Poland the deposits are of Cretaceous origin and contain up to 3·5% $Fe_2O_3$ and 7·0% $Al_2O_3$.[69]

## EUROPEAN DEPOSITS

European phosphate deposits are small in comparison with those of North Africa, the U.S.A. and the U.S.S.R., and are generally scattered. The location of the main phosphate-bearing regions has been previously described (Mellor, VIII, 735). Phosphate ores found in the British Isles are not of commercial value and occur as nodules and concretions and phosphatized fossils in geological strata dating back 350 million years. Near Bala in North Wales the phosphorites are in the form of black nodules associated with limestone formations. Phosphates of the Cretaceous period occur in isolated areas extending from the Isle of Wight to Yorkshire. They are found as nodules in the chalk beds and marl of Cambridgeshire and Bedfordshire, and in Sussex the chalk is occasionally phosphatized. In East Anglia the phosphate formations belong to the more recent Pliocene period and are largely composed of phosphatized fossils.[70] Marine phosphorites containing up to 28% $P_2O_5$ occur in Ireland in lenses and thin discontinuous layers.[71]

In Belgium and north-east France the deposits occur as phosphatic chalk and phosphate sand.[72] In south-western France the phosphates occur mixed with clay and are mostly derived from Jurassic limestones. Under the tropical conditions of the later Eocene period (about 50 million years ago) the clay became largely converted into hydrated alumina. This subsequently became phosphatized and the phosphatic clays accumulated in caverns in the limestone.[73] Phosphorites, both pure and mixed with red clay, quartz sand, bauxite and iron and manganese oxides occur as concretions in limestone pockets in the Bas-Languedoc district of south-eastern France.[74]

The Alentejo district of Portugal contains small deposits of apatites of igneous origin containing up to 10% $P_2O_5$.[75] Across the Spanish border similar ores are found in the Toledo mountains, associated with slate formations. They also occur in the Almeria district of south-eastern Spain.

In Austria, in the region of Linz, phosphorites containing up to 28% $P_2O_5$ are found in small quantities, mixed with sandstone, clay and dolomite.[76] To the north-west of this, at Auerbach in Germany, there is a deposit containing 20–24% $P_2O_5$, which appears to have originated in the reaction of limestone with decayed animal matter, which once accumulated in an isolated inlet of the sea.[77] A fluorapatite from Dalmatia in Yugoslavia has been reported.[78]

On the Swedish island of Gotland in the Baltic Sea there is a phosphorite conglomerate consisting of grey pebbles having a $P_2O_5$ content of 35%. Associated with this are phosphorite–sandstone pebbles, varying in colour from yellow to dark brown, which contain 12% $P_2O_5$.[79]

### OTHER AFRICAN DEPOSITS

South Africa has some phosphorite deposits in the form of lenses and nodular masses in the Laingsburg area of Cape Province. These contain 24–35% $P_2O_5$ and are believed to be chemical precipitates formed in shallow water.[80] Other districts of South Africa, including the Transvaal, also contain phosphates in the form of apatites, phosphate nodules and marine phosphorites. The $P_2O_5$ content of these varies from 10–41%, but most of the deposits are localized and are of little commercial importance.[81] Fluorapatite, containing $P_2O_5$ 41–43%, CaO 54–55%, and F 2·3–4·2%, is found associated with the pegmatites of the Kibaro–Urundian area of the eastern Congo in Central Africa.[82]

In Uganda there are large deposits of apatite minerals.[83] Amblygonite $[(Li,Na,Al)_4(PO_4,F,OH)_4,H_2O]$ associated with augelite $[Al_2(OH)_3PO_4]$, containing 36% $P_2O_5$ and 43% $Al_2O_3$, is mined at Mbale.[84] Apatite which by weathering on the surface has been converted into francolite occurs in Eastern Uganda.[85] This contains 41% $P_2O_5$, 55% CaO and 2·3% F.[86] Apatite is also found in the Sukulu mineral deposits of Uganda.[87] In the south-eastern region of the province, near Tororo, there is a weathered material which contains 13% $P_2O_5$ and 0·2% $Nb_2O_5$. The reserves of this have been estimated to be 130 million tons.[88]

The Thiès and Tivanouane regions of Senegal in French West Africa contain deposits of calcium phosphate averaging 34% $P_2O_5$ and 47% CaO, and of calcium aluminium phosphates averaging 34% $P_2O_5$ and 12% CaO.[89] The latter were formed by leaching of the phosphate from calcium phosphates and subsequent reaction with the underlying aluminous clays.[90] Crandallite $[CaAl_3(OH)_5(PO_4)_2H_2O]$ and augelite $[Al_2(OH)_3PO_4]$ are also found in this area.[91]

Deposits of sedimentary phosphates containing 12–43% $P_2O_5$ and estimated at 15 million tons have been located in Angola, Portuguese West Africa.[92] Very large deposits of high grade apatite ore have also been discovered in the northern part of the Spanish Sahara.[432]

### FAR EAST DEPOSITS

Apatite containing 20–25% $P_2O_5$ is found near Bihar in India.[93] In Trichinopoly and near Mussoorie there is a deposit in the form of nodules which contains 27% $P_2O_5$, 7% CaO and 2·5% F. The reserves are estimated at 8 million tons. Another deposit, also estimated at 8 million tons, occurs at Trichy in the form of phosphatic nodules. It contains on an average 25·6% $P_2O_5$. Conversion to superphosphate is uneconomical because of the high calcium carbonate content of the ore. Fusion with magnesium oxide and silica at 1500°C. converts it into a silicophosphate, the phosphorus of which is available to plants.[94, 433] The deposits at Mussoorie are of low to medium grade, but smaller deposits of higher grade ore occur at Jaisalmer in Rajasthan.[433]

Deposits of apatite having a very high phosphorus content have been reported to exist in Vietnam. Some of these are said to contain as much as 41% $P_2O_5$.[95] Two types of ore are present, one a sedimentary, micro-crystalline apatite and the other a weathered phosphate of limestone origin.[96]

The phosphate reserves of Japan have been estimated to be some 25 million tons and are found at Noto, Central Japan, where the $P_2O_5$ content is 33%. Other regions include Rasa Island and the Kita Daito Islands of the Okinawa group and the Palau or Pelew Islands to the east of the Philippines. Here the $P_2O_5$ content varies between 10 and 40% and between 29 and 40% respectively.[97] In South Japan some deposits contain 25–30% $P_2O_5$, but more usually the content is 15–20%. The fluorine present in the rock varies between 0·02 and 0·5%.[98]

Phosphate deposits containing 18–33% $P_2O_5$ and estimated to amount to about 18 million tons have been located in the Paracel Islands, Indo-China. They are said to have been formed by reaction of limestone with phosphate solutions derived from the leaching of guano.[23]

The phosphate resources of China do not seem to have been studied in any detail. Active mining operations take place in Kiang-Su province of Eastern China and guano occurs on Tungsha Island, south-east of Hong Kong.[97] In the Kiang-Su and An-Hwei regions to the north and north-west of Shanghai most of the rock is sedimentary and belongs to the late Cambrian period.[99] The phosphate, which does not seem to be pyrogenic in origin, rarely contains more than 30% $P_2O_5$. Some deposits contain 20% $P_2O_5$ but the more usual content is 8–15%.[100] The known ores of China have been estimated to be about 3 million tons.[4]

### AUSTRALASIAN DEPOSITS

Phosphate minerals in minor quantities occur in Australia. Phosphorites of secondary origin are found near Kapunda, apatite north of Adelaide and cretaceous phosphates at Dandarragan north of Perth.[97] The last occur as nodules in greensand and contain 12–17% $P_2O_5$.[101] Some apatites containing 27% $P_2O_5$ have also been found at Dandarragan.[102] Deposits of guano containing 4–27% $P_2O_5$ occur in the coastal areas of Western Australia between Perth and Dongara, 250 miles to the north, and on some islands off the east coast.[97] Xenotime, monazite and amblygonite ores containing 20–35% $P_2O_5$ are found in North-western Australia in the region of the Pilbara goldfields. Apatite associated with yttrium, lanthanum and other rare earths occurs in the New South Wales district.[103] A few deposits of phosphorite, mainly of academic interest, occur in New Zealand. North of Otago there is some phosphate rock containing 10–20% $P_2O_5$. Taranakite, vivianite and wavellite have also been found in South Auckland.

## Uranium in Phosphorus Minerals

Many phosphorites, phosphate minerals and rock contain uranium, the amount depending on the type of phosphate deposit, but usually being less than 0·2% $U_3O_8$. Fossil bones, however, may contain as much as 0·5% $U_3O_8$.

*Table IV.—Uranium in Phosphate Rock*
(p.p.m. $U_3O_8$)

| Source | $U_3O_8$ p.p.m. |
|---|---|
| Morocco, Algeria, Tunisia, Egypt | 40–160 |
| Florida, South Carolina | 10–1500 |
| Pacific, Indian and Caribbean Islands | 10–180 |
| British Isles | 30–1080 |
| Belgium, Germany, France, Spain | 10–70 |
| Nigeria | 40–110 |
| Russia, Norway, Uganda, South Africa | 10–300 |

The uranium content of phosphate rock and minerals has been determined by radiometric and chemical analysis, with the results shown in Table IV, which gives the parts per million found in deposits from various sources.[104]

Auto-radiographs suggested that the uranium in apatites was derived from the action of uranium-containing solutions, rather than from the magma from which the minerals were formed. The apatite structure has a greater geochemical affinity for uranium than has any other phase normally found during the dissolution or weathering of rocks.

Uranium occurs as an essential and major constituent of some twenty-two known phosphorus minerals (see Table XVI). These are mainly secondary minerals containing 15% or less of $P_2O_5$ and are formed by the weathering of ore deposits. They are less important as a possible source of uranium than the more abundant apatites and phosphorites. The uranium present in igneous rocks is most often found in or associated with apatite. It seems likely that the greater part of the uranium in the earth's crust is concentrated in apatites. Fluorapatite usually contains less than 0·01% $U_3O_8$, but in some igneous apatites this may be as high as 0·04%.[105] Although much apatite is used for the production of phosphorus and phosphates, it is not a suitable material for the easy recovery of uranium as a by-product.

All marine phosphorites contain some uranium, generally between 0·01 and 0·03% $U_3O_8$, but sometimes in amounts up to 0·2%. Since the greater part of world phosphate production uses marine phosphorites as raw material, they are a potential source of uranium as a by-product. The uranium is derived from sea water, either during deposition or by subsequent reaction with uranium-containing solutions.[106] This reaction is influenced by such factors as time, size of phosphorite grains and the permeability of the ore bed. Calcium, carbonate and hydroxyl ions hinder the removal of uranium from solution.[107] The Phosphoria formations of Wyoming and Northern Colorado, for example, contain up to 0·07% $U_3O_8$, the uranium content being very roughly proportional to the $P_2O_5$ and inversely proportional to the $CO_2$ in the phosphorite.[108] In the marine phosphorites the uranium is adsorbed on or is present in the lattice of the phosphate, the substitution mechanism probably involving isomorphous replacement of calcium by uranium.[109] Reducing conditions favour deposition of uranium in the phosphate, and in the lattice it is tetravalent. When adsorbed on apatite crystallites, however, the uranium is hexavalent and is present as the $UO_2^{2+}$ ion.[110] Because it is present in marine phosphorites in an acid-soluble form,[111] the uranium may be recovered as a by-product in the manufacture of superphosphate.[112] It is, however, more economical to carry out this recovery when the phosphorite is used for making wet-process phosphoric acid.[113]

Prolonged weathering of apatites and phosphorites, particularly under slightly acid conditions, can result in the decomposition of the phosphate. Where this has occurred in the presence of clay the apatite is converted to wavellite, $[(AlOH)_3(PO_4)_2,5H_2O]$, crandallite, $[CaAl_3(OH)_5(PO_4)_2,H_2O]$, and similar aluminium phosphate minerals.[114] This has happened with some of the Florida phosphate deposits[115] and with those in Senegal in Africa.[116, 91] In the latter instance the evidence is that uranium was initially present in apatite, from which an aluminium calcium phosphate was formed. During the primary phase of evolution of the deposits the uranium was retained in the mineral pallite, $[(AlFe)_{12}Ca_3(OH)_{18}(PO_4)_8,6H_2O]$. The latter under more recent climatic conditions became transformed by weathering into crandallite in which the uranium was concentrated.[117] Crandallite from this region contains 0·02–0·05% $U_3O_8$ and pallite 0·01–0·015%. In some of the North African phosphates of sedimentary origin the uranium content is 0·005–0·01% and appears to have been co-precipitated with the phosphate during the formation of the deposit.[118] The uranium content of aluminium phosphates which do not also contain calcium is negligible, presumably because the size of the aluminium ion is too small to allow substitution by the much larger uranium ion.

Guano phosphate deposits contain no uranium and the uranium content of phosphatized rock and river pebble phosphate deposits is usually very low. Fossil bones are an interesting example of the affinity of apatite for uranium. Ordinary bone, which is mainly carbonate-apatite, contains no uranium, but in fossil bones the uranium content increases with age. When associated with phosphorites, fossil bones usually have the same uranium content as the phosphorite. In some instances, however, particularly with isolated bone piles, the uranium content may be quite high. For example, fossil bones from the old red sandstone formations contain as much as 0·55% $U_3O_8$.[104] In the Salt Wash sandstone in the U.S.A. fossilized dinosaur bones have acted as a nucleus around which uranium has precipitated during mineralization.[119]

## Minor and Trace Elements in Phosphorites

As many as thirty-two elements have been found to be present in phosphate rock in trace amounts.[120, 427] Some of these are important because of the possibility of recovering sizeable amounts of the element from the vast quantities of phosphate ores used for the manufacture of phosphorus, phosphoric acid and phosphates. They may also be significant as trace elements in the fertilizing action of phosphorites when directly applied to the soil.

*Table V.—Minor Metallic Constituents of Phosphate Rock*

| Source | Metallic constituent in p.p.m. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Na_2O$ | $K_2O$ | CuO | ZnO | MgO | MnO | $Cr_2O_3$ | $V_2O_3$ | $TiO_2$ | $As_2O_3$ |
| Florida | 0–7000 | 500–5000 | 0–30 | 0–120 | 0–8500 | 0–500 | 0–400 | 0–200 | 300–3500 | 0–50 |
| Tennessee | 1300–4000 | 400–6000 | 0–40 | 0–10 | 600–5500 | 0–3000 | 0–100 | 0–100 | 400–900 | 10–40 |
| Western States | 1600–8000 | 2000–6000 | 30–110 | 0–10 | 0–3000 | 0–300 | 500–1500 | 400–4000 | 400–1000 | 10–140 |
| South Carolina | 3000–4000 | 2000–3000 | 50 | 0–5 | 3000–4000 | 300–900 | 300 | 0 | 700–800 | 5 |
| Morocco | 11,900 | 1,600 | — | — | 1,600 | 20 | 400 | 0 | 250 | — |
| Tunis | 12,500 | 4,400 | — | — | 4,500 | 30 | 450 | 0 | 500 | — |
| Curacao | 8,800 | 900 | — | — | 12,300 | 30 | 50 | 100 | 200 | — |

The amounts of some minor metallic constituents of phosphate rock from the U.S.A., North African and West Indies deposits are given in Table V. The $P_2O_5$ content of the samples which were examined was between 27 and 39%, except for one or two specimens from Florida and Tennessee, which contained 21 and 11% $P_2O_5$, respectively.[121]

*Table VI.—Trace Elements in United States Phosphate Rock*

| | Florida p.p.m. | Tennessee p.p.m. | Western p.p.m. |
|---|---|---|---|
| $As_2O_5$ | 2–30 | 7–75 | 6–140 |
| BaO | — | 100–300 | 500–900 |
| $B_2O_3$ | 20–100 | 35–75 | 20–70 |
| $Cr_2O_3$ | 1–130 | 30–70 | 500–1300 |
| CuO | 5–30 | 20–30 | 30–100 |
| I | 5–130 | 10–30 | 1–3 |
| MnO | 20–500 | 700–3000 | 20–500 |
| $MoO_3$ | 20–100 | 1–5 | 15–250 |
| NiO | 20–100 | 1–10 | — |
| N | 50–200 | 40–250 | 80–1100 |
| Rare earths $R_2O_3$ | 100–700 | 100–200 | 500–1800 |
| $SeO_3$ | 0–15 | 15–100 | 15–100 |
| SrO | 1000 | — | — |
| $SnO_2$ | 10–50 | 5–50 | — |
| $TiO_2$ | 300–700 | 500–2000 | 400–1000 |
| $U_3O_8$ | 100–300 | 5–20 | 50–100 |
| $V_2O_3$ | 10–200 | 0–100 | 400–4000 |
| ZnO | 0–5 | 0–10 | 0–250 |

The minor constituents of phosphate deposits in other parts of the world are probably similar to those shown above. In the case of lower grade ores, however, some modification is to be expected owing to the variations in composition and type of rock formation in contact with the phosphorite. For example, the phosphorite nodules in the Podolia region of the Dniester river in the U.S.S.R. are sulphide-bearing ores. They are characterized by intergrowths of galena, sphalerite and globules of pyrite and chalcopyrite. The phosphorite is a typical fluorapatite containing 20–35% $P_2O_5$, 1·8% $CO_2$ and 2·5–3·5% F, together with several per cent of copper, zinc and lead. It also contains traces of lithium, silver, cadmium, tin, selenium, nickel, cobalt, zirconium, yttrium and ytterbium.[122]

A number of phosphorites have been found to contain rare-earth elements in small quantities. The Kara-Tau deposits of the U.S.S.R. contain 0·13% of rare earth oxides, mostly yttrium, but also some lanthanum, cerium and ytterbium.[123] The phosphate rock from Ocean Island in the South Pacific contains about 60 p.p.m. of rare earths, mainly cerium, neodymium, lanthanum and praseodymium. The neighbouring Nauru Island phosphate contains none of these elements. The difference is attributed to metamorphism of the Nauru rock.[124]

More recent data on the trace elements in phosphate rock found in the U.S.A. have been collected together by Van Wazer.[4] A summary is given in Table VI, the information referring to the Florida, Tennessee and Western States deposits, containing 20–35% $P_2O_5$.

Florida rock may also contain up to 100 p.p.m. of beryllium, cadmium, cæsium, lead, lithium, mercury, rubidium, silver and zirconium.

## THERMODYNAMIC PROPERTIES OF APATITES

The heat capacities of calcium fluorapatite and of calcium hydroxyapatite have been determined in the temperature range 15–1500°K. These measurements were made on synthetic materials. Calcium hydroxyapatite was prepared according to the procedure of Rathje.[125] 0·2 M. aqueous calcium nitrate and 0·12 M. aqueous mono-ammonium phosphate were added at a rate of 100 ml./hr. to water at 95°C. The mixture was stirred and the pH kept at 4·5 (bromophenol blue indicator) by addition of ammonium hydroxide. After settling, filtering and washing, the precipitate was dried at 110°C. and then heated for 72 hr. at 950°C. in an atmosphere containing 20% of water vapour, to promote crystallization. The equation for the reaction is:

$$10Ca(NO_3)_2 + 6NH_4H_2PO_4 + 14NH_4OH \\ = Ca_{10}(OH)_2(PO_4)_6 + 20NH_4NO_3 + 12H_2O$$

The product contained 42·38% $P_2O_5$ and 55·68% CaO as compared with theoretical values of 42·39% and 55·80% respectively. There was also present 0·30% $Al_2O_3$.

Calcium fluorapatite was made by heating a mixture of tricalcium phosphate and calcium fluoride. $\beta$-Calcium metaphosphate was first prepared by slowly heating to 500°C. monocalcium phosphate which had been recrystallized from hot phosphoric acid solution. Tricalcium phosphate was then made by heating for 5 hr. at 1150°C. a stoicheiometric mixture of the calcium metaphosphate and calcium carbonate which had been precipitated by ammonium carbonate from a hot solution of recrystallized calcium nitrate. Calcium fluoride was made by neutralizing hydrofluoric acid with calcium carbonate. Finally a stoicheiometric mixture of tricalcium phosphate and calcium fluoride was heated for 30 min. at 1370°C. in an atmosphere of nitrogen and in the presence of calcium fluoride vapour to prevent loss of fluorine. The product contained 42·20% $P_2O_5$, 55·60% CaO and 3·75% F, as compared with theoretical values of 42·22%, 55·60% and 3·77%, respectively. There were also present 0·02% MgO, 0·03% $SiO_2$ and 0·12% SrO. Microscopical examination showed that the material contained less than 0·1% of unreacted calcium fluoride. The purity of both products was also checked by *X*-ray examination and they were found to be identical with naturally occurring apatites. It was also confirmed that their structure and composition were unchanged after heating to 1500°K.

The experimental values of the low temperature heat capacities, in g.-calories per mole, are given in Table VII and Table VIII.

*Table VII.—Heat Capacity of Calcium Hydroxyapatite* ($Ca_{10}(PO_4)_6(OH)_2$) *in the Temperature Range* 15–298·16°K.[126]

| Temp. $T$°K. | $C_p$ g.-cal./mole | Temp. $T$°K. | $C_p$ g.-cal./mole | Temp. $T$°K. | $C_p$ g.-cal./mole |
|---|---|---|---|---|---|
| 15 | 1·10 | 115 | 90·57 | 215 | 152·3 |
| 20 | 2·32 | 120 | 94·54 | 220 | 154·5 |
| 25 | 4·76 | 125 | 98·39 | 225 | 156·7 |
| 30 | 7·76 | 130 | 102·2 | 230 | 158·7 |
| 35 | 11·36 | 135 | 105·9 | 235 | 160·8 |
| 40 | 15·35 | 140 | 109·4 | 240 | 162·9 |
| 45 | 19·57 | 145 | 112·9 | 245 | 164·9 |
| 50 | 23·94 | 150 | 116·2 | 250 | 167·0 |
| 55 | 28·76 | 155 | 119·5 | 255 | 168·9 |
| 60 | 34·75 | 160 | 122·7 | 260 | 170·8 |
| 65 | 41·22 | 165 | 125·8 | 265 | 172·7 |
| 70 | 47·22 | 170 | 128·8 | 270 | 174·5 |
| 75 | 52·75 | 175 | 131·6 | 275 | 176·3 |
| 80 | 57·88 | 180 | 134·4 | 280 | 177·9 |
| 85 | 63·01 | 185 | 137·1 | 285 | 179·7 |
| 90 | 68·17 | 190 | 139·8 | 290 | 181·4 |
| 95 | 73·14 | 195 | 142·5 | 295 | 183·1 |
| 100 | 77·83 | 200 | 145·0 | 298·16 | 184·07 |
| 105 | 82·30 | 205 | 147·6 | | |
| 110 | 86·49 | 210 | 150·0 | | |

The high temperature heat capacity of calcium hydroxyapatite for the temperature range 298–1500°K. is given by the following equation:

$$C_p = 228{\cdot}52 + 39{\cdot}62 \times 10^{-3}T - 50 \times 10^{5}T^{-2} \text{ g.-cal./mole} \pm 0{\cdot}22\%$$

The equations for the heat content and entropy, as derived from the heat capacity equation, are:

$$H_T - H_{298} = 228{\cdot}52T + 19{\cdot}81 \times 10^{-3}T^2 + 50 \times 10^{5}T^{-1} - 86{,}670 \text{ g.-cal./mole}$$
$$S_T - S_{298} = 526{\cdot}19 \log T + 39{\cdot}62 \times 10^{-3}T + 25 \times 10^{5}T^2 - 1342 \text{ g.-cal./mole/degree}$$

*Table VIII.—Heat Capacity of Calcium Fluorapatite* ($Ca_{10}(PO_4)_6F_2$) *in the Temperature Range* 15–298·16°K.[127]

| Temp. $T$°K. | $C_p$ g.-cal./mole | Temp. $T$°K. | $C_p$ g.-cal./mole | Temp. $T$°K. | $C_p$ g.-cal./mole |
|---|---|---|---|---|---|
| 15 | 0·98 | 115 | 90·32 | 215 | 149·7 |
| 20 | 2·47 | 120 | 94·33 | 220 | 151·8 |
| 25 | 4·81 | 125 | 98·18 | 225 | 153·8 |
| 30 | 7·87 | 130 | 101·9 | 230 | 155·8 |
| 35 | 11·67 | 135 | 105·5 | 235 | 157·8 |
| 40 | 15·86 | 140 | 109·0 | 240 | 159·8 |
| 45 | 20·51 | 145 | 112·3 | 245 | 161·7 |
| 50 | 25·65 | 150 | 115·6 | 250 | 163·6 |
| 55 | 31·01 | 155 | 118·7 | 255 | 165·4 |
| 60 | 36·58 | 160 | 121·8 | 260 | 167·2 |
| 65 | 42·08 | 165 | 124·7 | 265 | 168·9 |
| 70 | 47·47 | 170 | 127·6 | 270 | 170·6 |
| 75 | 52·73 | 175 | 130·3 | 275 | 172·2 |
| 80 | 58·03 | 180 | 132·9 | 280 | 173·9 |
| 85 | 63·22 | 185 | 135·5 | 285 | 175·6 |
| 90 | 68·15 | 190 | 138·0 | 290 | 177·2 |
| 95 | 72·87 | 195 | 140·5 | 295 | 178·8 |
| 100 | 77·42 | 200 | 142·9 | 298·16 | 179·73 |
| 105 | 81·85 | 205 | 145·3 | | |
| 110 | 86·16 | 210 | 147·5 | | |

To obtain the heat content and entropy referred to the absolute zero of temperature the following values should be added to those calculated from the above equations:

$$H_{298}-H_0 = 30{,}710 \text{ g.-cal./mole}$$
$$S_{298}-S_0 = 186{\cdot}6 \text{ g.-cal./mole/degree}$$

The heat capacity, heat content and entropy equations for calcium fluorapatite in the temperature range 15–1600°K. are as follows:

$$C_p = 226{\cdot}04+28{\cdot}88\times10^{-3}T-48{\cdot}82\times10^5T^{-2} \text{ g.-cal./mole}$$
$$H_T-H_{298} = 226{\cdot}04T+14{\cdot}44\times10^{-3}T^2+48{\cdot}82\times10^5T^{-1}-85{,}050 \text{ g.-cal./mole}$$
$$S_T-S_{298} = 520{\cdot}48\log T+28{\cdot}88\times10^{-3}T+24{\cdot}41\times 10^5T^2-1324 \text{ g.-cal./mole/degree}$$

*Table IX.—Heat Content and Entropy of Calcium Hydroxyapatite* ($Ca_{10}(PO_4)_6(OH)_2$) *in the Temperature Range* 298–1500°K.

| Temp. $T$°K. | Heat content $H_T$–$H_{298}$ g.-cal./mole | Entropy $S_T$–$S_{298}$ g.-cal./mole/degree |
|---|---|---|
| 298 | 0 | 0 |
| 400 | 20,340 | 58·7 |
| 500 | 42,690 | 108·0 |
| 600 | 66,000 | 150·5 |
| 700 | 90,010 | 187·5 |
| 800 | 114,710 | 220·5 |
| 900 | 140,090 | 250·3 |
| 1000 | 166,130 | 277·8 |
| 1100 | 192,780 | 303·2 |
| 1200 | 220,050 | 326·9 |
| 1300 | 247,890 | 349·2 |
| 1400 | 276,280 | 370·2 |
| 1500 | 305,180 | 390·1 |

*Table X.—Heat Content and Entropy of Calcium Fluorapatite* ($Ca_{10}(PO_4)_6F_2$) *in the Temperature Range* 298–1600°K.

| Temp. $T$°K. | Heat content $H_T$–$H_{298}$ g.-cal./mole | Entropy $S_T$–$S_{298}$ g.-cal./mole/degree |
|---|---|---|
| 298 | 0 | 0 |
| 400 | 20,100 | 57·5 |
| 500 | 41,700 | 104·9 |
| 600 | 64,060 | 145·9 |
| 700 | 86,490 | 181·3 |
| 800 | 110,790 | 214·2 |
| 900 | 135,650 | 242·7 |
| 1000 | 159,710 | 268·6 |
| 1100 | 185,720 | 293·0 |
| 1200 | 211,140 | 315·0 |
| 1300 | 237,310 | 335·9 |
| 1400 | 263,810 | 355·3 |
| 1500 | 290,130 | 373·4 |
| 1600 | 315,000 | 389·6 |

The heat content and entropy referred to the absolute zero of temperature are found by adding the following values to those derived from the above equations:

$$H_{298}-H_0 = 30{,}340 \text{ g.-cal./mole}$$
$$S_{298}-S_0 = 185{\cdot}5 \text{ g.-cal./mole/degree}$$

The actual experimental data found for the heat content and entropy of the two materials in the temperature range 298–1500°K. are shown in Table IX and Table X.

The calcium hydroxyapatite was not heated above 1472°K. because of slight decomposition occurring. The values for 1500°K. were therefore extrapolated, but were considered to be reasonably accurate.

The heats of formation of calcium fluorapatite, hydroxyapatite and chlorapatite have been determined by measuring the heats of reaction of these compounds with 20% and 30% nitric acid solution.[128] Calcium fluorapatite was prepared by a slight modification of the method of Egan, Wakefield and Elmore.[127] The purity was 97%. Calcium hydroxyapatite was made by neutralizing with ammonium hydroxide to pH 12 a 5% solution of diammonium phosphate. To this there was then added, with stirring, the stoicheiometric quantity of a 20% solution of calcium nitrate, also neutralized to pH 12 with ammonium hydroxide. The mixture was boiled for 10 min., filtered, washed and the product dried at 250°C. to remove traces of ammonium nitrate. It was then heated at 800°C. for a short time.[129] The material had a purity of 98·5%. Calcium chlorapatite was prepared by heating a stoicheiometric mixture of tricalcium phosphate and calcium chloride for 12 hr. at 800–900°C. in a stream of dry nitrogen.[130] The purity was 98·5%.

The mean values of the heats of formation were:

Fluorapatite = −3262 kcal./mole
Chlorapatite = −3171 kcal./mole
Hydroxyapatite = −3231 kcal./mole.

These values were estimated to be correct to within ±0·07%. The impurities in the materials were considered to be calcium fluoride and tricalcium phosphate in the fluorapatite, calcium pyrophosphate in the hydroxyapatite, and calcium chloride and tricalcium phosphate in the chlorapatite. The effect of these would be to lower the above heats of formation by 1·8 kcal./mole for fluorapatite and by 0·5 and 1·0 kcal./mole, respectively, for the hydroxy- and chlorapatite. A more recent estimate[131] has put the heat of formation of calcium fluorapatite at −3267·2±0·4 kcal./mole.

Careful examination of the mechanism involved when calcium fluorapatite is dissolved in 30% nitric acid revealed that the reaction might not take place according to the simple equation:

$$3Ca_3(PO_4)_2{,}CaF_2+14HNO_3+3H_2O = 3Ca(H_2PO_4)_2{,}H_2O+7Ca(NO_3)_2+2HF$$

Monocalcium phosphate did not precipitate from 30% nitric acid solution and there was no evidence to support the conclusion that other calcium phosphates or fluorophosphates were absent. It was also possible that some interaction occurred between calcium nitrate, calcium phosphates and hydrogen fluoride in solution.

To avoid having to make assumptions as to the compounds in solution and possible reactions among them, heats of reaction were measured for the following changes:

1. $3Ca_3(PO_4)_2{,}CaF_2+14HNO_3 = 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+2HF$
2. $3Ca_3(PO_4)_2+CaF_2+14HNO_3 = 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+2HF$
3. $6H_3PO_4+CaF_2+9Ca(OH)_2+14HNO_3 = 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+2HF+18H_2O$
4. $6H_3PO_4+CaF_2+9CaO+14HNO_3 = 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+2HF+9H_2O$.

The experiments were carried out in 31 wt.-% nitric acid and in a mixture containing 31% nitric acid and 0·10 M. phosphoric acid. The heat of mixing nitric and phosphoric acids in the proportions used for equations 3 and 4 was also determined. By eliminating undetermined quantities from these measurements, three independent values of −3298, −3294 and −3295, average −3296±2·5 kcal./mole, were obtained for the heat of formation of calcium fluorapatite. The latter was a sample of natural fluorapatite containing 40·9% $P_2O_5$, 54·8% CaO, 2·2% F, 0·09% Cl, 0·86% $Al_2O_3$, 0·41% $Fe_2O_3$ and 0·19% MgO.

Similar determinations were made on a sample of calcium hydroxyapatite prepared by calcining human teeth at 800°C. *X*-Ray examination indicated a very pure apatite structure with a trace of tricalcium phosphate. The product contained 0·15% of fluorine, equivalent to 4·2% of calcium fluorapatite. The heats of the following reactions were measured:

$$\begin{aligned}
3Ca_3(PO_4)_2,Ca(OH)_2+14HNO_3 &= 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+2H_2O\\
3Ca_3(PO_4)_2+Ca(OH)_2+14HNO_3 &= 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+2H_2O\\
6H_3PO_4+10Ca(OH)_2+14HNO_3 &= 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+20H_2O\\
10CaO+6H_3PO_4+14HNO_3 &= 3Ca(H_2PO_4)_2+7Ca(NO_3)_2+10H_2O
\end{aligned}$$

These determinations gave three values of $-3229\pm2{\cdot}7$ kcal./mole for the heat of formation of calcium hydroxyapatite.[132]

Another value for the heat of formation of calcium fluorapatite is $-3269$ kcal./mole at 25°C. This figure was obtained for a naturally-occurring apatite from the Kola Peninsula, U.S.S.R., and for a synthetic apatite which was prepared by heating for 4 hr. at 900°C. a stoicheiometric mixture of calcium fluoride, calcium oxide and dicalcium phosphate. The Kola apatite contained 41·5% $P_2O_5$ and 52·5% CaO, and the analysis of the synthetic material was: 42·2% $P_2O_5$, 55·6% CaO and 3·76% F.[133]

The heat of formation at 25°C. of calcium hydroxyapatite made by the procedure described above (p. 12)[125–6] was found to be $-3212$ kcal./mole.[133]

The thermodynamic properties of berlinite ($AlPO_4$) have been determined,[134] with the results shown in Table XI.

*Table XI.—The Thermodynamic Properties of Berlinite* ($AlPO_4$)[134]

| Temp. °K. | (Units g.-cal., mole, degree) | | | Temp. °K. | (Units g.-cal., mole, degree) | | |
|---|---|---|---|---|---|---|---|
| | $C_p$ | $S^\circ_T$ | $H^\circ_T-H^\circ_0$ | | $C_p$ | $S^\circ_T$ | $H^\circ_T-H^\circ_0$ |
| 10 | 0·031 | 0·006 | 0·049 | 160 | 13·48 | 10·66 | 1016 |
| 15 | 0·186 | 0·045 | 0·548 | 170 | 14·26 | 11·50 | 1155 |
| 20 | 0·456 | 0·132 | 2·098 | 180 | 15·02 | 12·34 | 1301 |
| 25 | 0·858 | 0·275 | 5·336 | 190 | 15·74 | 13·17 | 1455 |
| 30 | 1·340 | 0·473 | 10·81 | 200 | 16·43 | 14·00 | 1616 |
| 35 | 1·857 | 0·718 | 18·80 | 210 | 17·10 | 14·82 | 1784 |
| 40 | 2·393 | 1·001 | 29·42 | 220 | 17·75 | 15·63 | 1958 |
| 45 | 2·934 | 1·314 | 42·74 | 230 | 18·39 | 16·43 | 2139 |
| 50 | 3·473 | 1·615 | 58·76 | 240 | 19·00 | 17·23 | 2325 |
| 60 | 4·505 | 2·376 | 98·69 | 250 | 19·64 | 18·01 | 2519 |
| 70 | 5·505 | 3·147 | 148·8 | 260 | 20·17 | 18·79 | 2718 |
| 80 | 6·500 | 3·946 | 208·8 | 270 | 20·73 | 19·56 | 2922 |
| 90 | 7·454 | 4·768 | 278·6 | 280 | 21·29 | 20·33 | 3132 |
| 100 | 8·353 | 5·599 | 357·6 | 290 | 21·83 | 21·09 | 3348 |
| 110 | 9·250 | 6·438 | 445·7 | 300 | 22·37 | 21·83 | 3569 |
| 120 | 10·13 | 7·281 | 542·6 | | | | |
| 130 | 11·00 | 8·126 | 648·3 | 273·16 | 20·91 | 19·81 | 2988 |
| 140 | 11·85 | 8·973 | 762·6 | 298·16 | 22·27 | 21·70 | 3528 |
| 150 | 12·69 | 9·820 | 885·3 | | | | |

The berlinite used in these measurements was a synthetic material made by reacting 1·92 mole of sodium aluminate with 1 litre of 8 M. phosphoric acid:

$$NaAlO_2+2H_3PO_4 = AlPO_4+NaH_2PO_4+2H_2O$$

The material was crystallized from phosphoric acid in an autoclave at 132–315°C.[135] It contained 58·23% $P_2O_5$ and its optical and *X*-ray properties agreed with those of the naturally-occurring mineral.[134] The entropy of variscite ($AlPO_4,2H_2O$) was estimated to be 40·5 g.-cal./mole/degree.[134]

The thermodynamic properties of potassium taranakite, $K_3H_6Al_5(PO_4)_8,18H_2O$, and of ammonium taranakite, $(NH_4)_3H_6Al_5(PO_4)_8,18H_2O$, are given in Table XII.

The heat and entropy of formation of potassium and ammonium taranakite from their elements at 25°C. are shown in Table XIII.

*Table XII.—Thermodynamic Properties of Potassium and Ammonium Taranakite*[136]

| Temp. °K. | $K_3H_6Al_5(PO_4)_8.18H_2O$ (Units g.-cal., mole, degree) | | | $(NH_4)_3H_6Al_5(PO_4)_8.18H_2O$ (Units g.-cal., mole, degree) | | |
|---|---|---|---|---|---|---|
| | $C_p$ | $S^\circ_T$ | $H^\circ_T-H^\circ_0$ | $C_p$ | $S^\circ_T$ | $H^\circ_T-H^\circ_0$ |
| 10 | 0·841 | 0·282 | 2·108 | 0·673 | 0·323 | 2·169 |
| 15 | 2·845 | 0·947 | 10·63 | 1·977 | 0·796 | 8·213 |
| 20 | 6·801 | 2·260 | 33·93 | 4·997 | 1·737 | 24·93 |
| 25 | 12·55 | 4·366 | 81·64 | 9·618 | 3·321 | 60·86 |
| 30 | 19·60 | 7·262 | 161·6 | 15·58 | 5·580 | 123·2 |
| 35 | 27·41 | 10·86 | 278·9 | 22·41 | 8·480 | 217·7 |
| 40 | 35·66 | 15·06 | 436·4 | 29·98 | 11·96 | 348·5 |
| 45 | 44·02 | 19·74 | 635·6 | 37·91 | 15·95 | 518·1 |
| 50 | 52·42 | 24·81 | 876·7 | 46·09 | 20·36 | 728 |
| 60 | 69·08 | 35·84 | 1484 | 62·67 | 30·23 | 1272 |
| 70 | 85·36 | 47·74 | 2277 | 79·42 | 41·15 | 1982 |
| 80 | 101·2 | 60·16 | 3190 | 96·02 | 52·83 | 2859 |
| 90 | 116·0 | 72·94 | 4277 | 112·3 | 65·09 | 3902 |
| 100 | 129·9 | 85·89 | 5507 | 127·9 | 77·74 | 5103 |
| 110 | 143·5 | 98·91 | 6874 | 143·1 | 90·64 | 6458 |
| 120 | 156·8 | 112·0 | 8376 | 158·2 | 103·7 | 7964 |
| 130 | 170·0 | 125·0 | 10010 | 172·8 | 117·0 | 9620 |
| 140 | 182·8 | 138·1 | 11770 | 181·4 | 130·3 | 11420 |
| 150 | 195·2 | 151·2 | 13660 | 201·4 | 143·7 | 13370 |
| 160 | 207·2 | 164·1 | 15680 | 215·3 | 157·2 | 15450 |
| 170 | 219·1 | 177·1 | 17810 | 228·8 | 170·6 | 17670 |
| 180 | 230·6 | 189·9 | 20060 | 242·0 | 184·1 | 20020 |
| 190 | 241·7 | 202·7 | 22420 | 255·0 | 197·5 | 22510 |
| 200 | 252·9 | 215·4 | 24890 | 268·0 | 210·9 | 25120 |
| 210 | 264·1 | 228·0 | 27480 | 281·1 | 224·3 | 27870 |
| 220 | 274·8 | 240·5 | 30170 | 293·6 | 237·7 | 30740 |
| 230 | 285·2 | 252·9 | 32970 | 305·5 | 251·0 | 33740 |
| 240 | 295·8 | 265·3 | 35880 | 317·3 | 264·2 | 36850 |
| 250 | 306·1 | 277·6 | 38890 | 328·3 | 277·4 | 40080 |
| 260 | 316·0 | 290·0 | 42000 | 340·0 | 290·6 | 43430 |
| 270 | 325·9 | 301·9 | 45210 | 350·9 | 303·6 | 46880 |
| 280 | 335·9 | 313·9 | 48520 | 361·6 | 316·6 | 50450 |
| 290 | 345·9 | 325·9 | 51920 | 372·1 | 329·4 | 54110 |
| 300 | 356·2 | 337·8 | 55430 | 382·4 | 342·2 | 57890 |
| 273·16 | 329·0 | 305·7 | 46240 | 354·3 | 307·7 | 48000 |
| 298·16 | 354·3 | 335·6 | 54780 | 380·5 | 339·9 | 57185 |

*Table XIII.—Heat and Entropy of Formation at 25°C. of Potassium and Ammonium Taranakite*[136]

| Product | $\Delta H^\circ_f$ at 25°C. kcal./mole | $\Delta S^\circ_f$ at 25°C. g.-cal./mole/degree |
|---|---|---|
| $K_3H_6Al_5(PO_4)_8,18H_2O$ | −4523·2 ± 5 | 335·6 ± 0·6 |
| $(NH_4)_3H_6Al_5(PO_4)_8,18H_2O$ | −4432·5 ± 5 | 339·9 ± 0·6 |

*Table XIV.—Heat and Entropy of Formation of Water and Various Ions at 25°C.*[136]

| | $\Delta H^\circ_f$ kcal./mole | $\Delta S^\circ_f$ g.-cal./mole/degree |
|---|---|---|
| $H_2O$ (l) | −68·317 | 16·72 |
| $H^+$ aq. | 0 | 0 |
| $K^+$ aq. | −60·04 | 24·5 |
| $NH_4{}^+$ aq. | −31·74 | 26·97 |
| $Al^{3+}$ aq. | −125·4 | −74·9 |
| $PO_4{}^{3-}$ aq. | −306·9 | −52 |

From the data given above and those of Table XIV the heat of solution in water at 25°C. was calculated to be 31·14 kcal./mole for potassium taranakite and 27·32 kcal./mole for the ammonium compound. The corresponding entropies of solution were −751·7 g.-cal./mole/degree and −748·5 g.-cal./mole/degree, respectively.

The solubility product constant derived from:

$$R - T \ln K_{\text{sp}} = \Delta H_{(\text{aq.}-\text{c})} - T\Delta S_{(\text{aq.}-\text{c})}$$

gave values for $\text{p}K_{\text{sp}}$ of 187·1 and 183·7 for the potassium and ammonium compounds, respectively. The measured values were 178·7 for potassium taranakite and 175·5 for the ammonium salt.[137] These values were considered to be apparent, rather than true, thermodynamic figures, because of the presence of complex ions in solution.

The potassium taranakite used in all the above measurements was made by dissolving 21·6 g. of aluminium in 870 ml. of 53·5% phosphoric acid, filtering and diluting to 2 l. After adjusting to pH 3·4 with 10% potassium hydroxide and diluting to 3·5 l., the solution was digested at 50°C. for 24 hr. The crystals were dried over calcium chloride in a vacuum at room temperature. The analysis was 56·6% $P_2O_5$, 9·6% Al and 8·6% K.

The ammonium salt was made in a similar way except that the aluminium phosphate was neutralized to pH 4 with 28% ammonium hydroxide. The product contained 59·6% $P_2O_5$, 10·5% Al and 4·1% $NH_4$.[137]

## PHOSPHORUS MINERALS

Phosphorus occurs in minerals in combination with some thirty other elements, the ores of commercial value generally being either fluorapatite or hydroxyapatite. There are, however, many phosphate deposits which are not distinctly crystalline like apatite, but occur as fibrous or compact masses or in the form of nodules. These are usually lower grade ores which contain little or no fluorine and in which the calcium oxide is generally not distributed in a regular manner throughout the lattice as it is in apatite. Such minerals have been given the name *phosphorite*, a term which was originally used to describe a Spanish mineral which phosphoresced when heated. In many instances, however, the distinction between apatite and phosphorite is not precise, the structures of both often being very similar.

Apatite, which is the most important of the phosphorus minerals, shows a wide variety of appearance. The crystals may be opaque or transparent, white or colourless, or various shades of yellow, green, blue, violet or brown. The crystal form is hexagonal and exhibits pyramidal hemihedrism, apatite being the best example of this type of symmetry.

The crystal structure of the apatites enables a large number and variety of substitutions to occur, particularly isomorphous replacement among similar ions. Because of this it is not possible to give a satisfactory general formula which would indicate all the possible substitutions which may arise. For most purposes, however, the unit cell of the crystal may be represented as $M_{10}X_2(RO_4)_6$.[138] In this formula M can be lithium, sodium, potassium, the alkaline earth metals, lead, magnesium, zinc, cadmium, iron, manganese, aluminium, copper, uranium or the rare earths. X may be fluorine, chlorine, bromine, the hydroxyl ion and possibly carbonate. R is generally phosphorus or arsenic, but may be sulphur, silicon or vanadium, and, more rarely, chromium or boron.

Apatites are usually grouped into two classes, each having distinct characteristics but possessing the same type of structure. In one of these, generally referred to as the apatite series, the dominant cation is calcium and the unit cell dimensions are approximately $a_0 = 9{\cdot}4$ A. and $c_0 = 6{\cdot}9$ A. The major anions are hydroxyl and fluoride and a wide range of substitutional solid solutions can occur in the series.

In the other, known as the pyromorphite series, lead is the dominant cation and the unit cell dimensions are a little larger, with $a_0 = 10{\cdot}2$ A. and $c_0 = 7{\cdot}5$ A. approximately.

The major anion in this series is chloride and there are no analogues of hydroxyapatite or fluorapatite.

Silicon and sulphur can replace phosphorus in the apatite series of minerals, while arsenic and vanadium are not usually present in large amounts. Calcium is not replaced by lead to any extent in the apatites. In the pyromorphite series on the other hand substitution of silicon and sulphur for phosphorus occurs to a lesser extent, whereas almost complete replacement of phosphorus by arsenic and vanadium can occur. Calcium does not often replace lead.

## The Structure of Apatite

The first descriptions of the apatite structure were given by Náray-Szabó[139] and by Mehmel.[140] The structures determined by both authors were very similar, differing only in the positions assigned to the fluorine atoms. It was said that the structure proposed by Mehmel applied to chlorapatite, while that described by Náray-Szabó was applicable to fluorapatite and hydroxyapatite.[141]

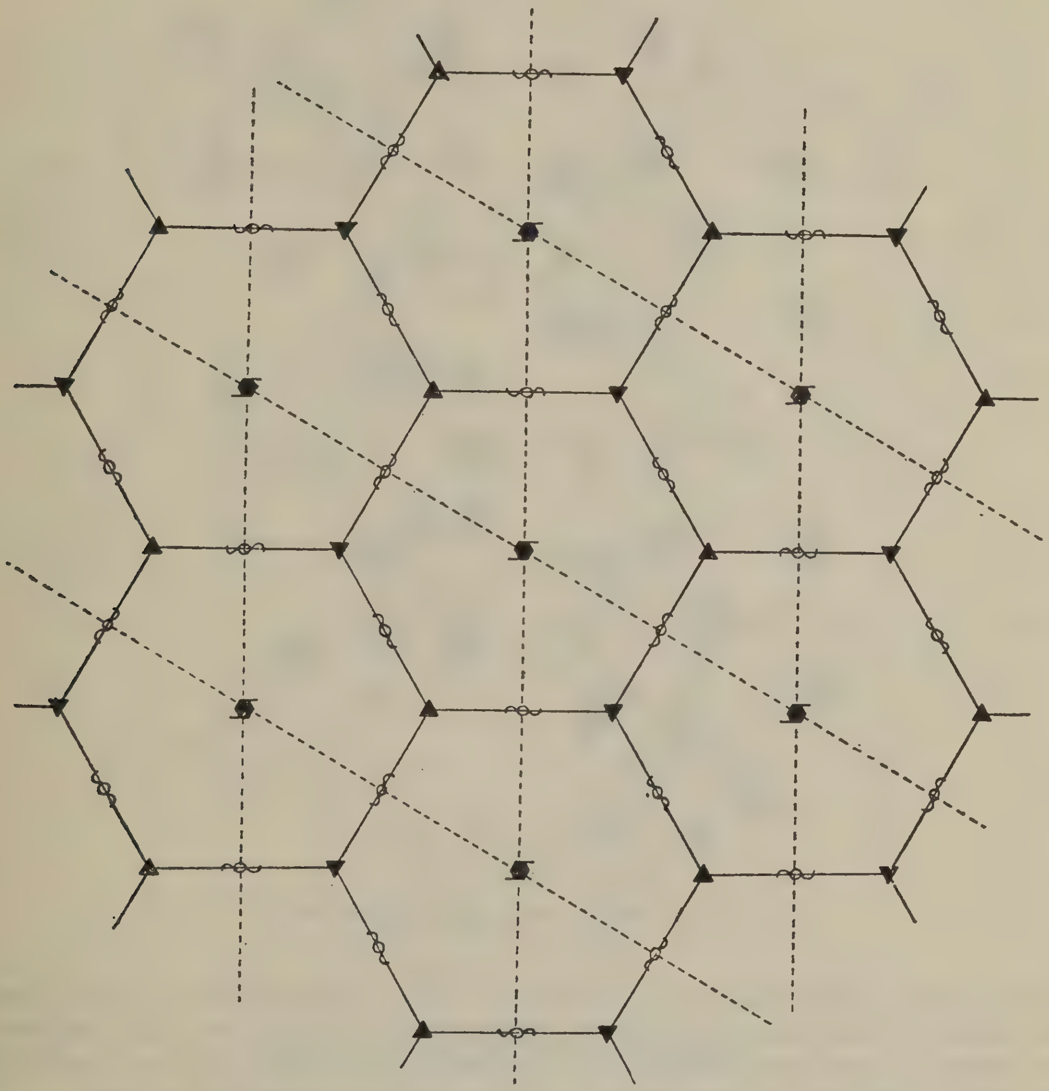


FIG. 1.—The arrangement of the vertical symmetry-axes in the apatite structure. The dotted lines show the hexagonal *a*-axes of reference.

The structure of calcium fluorapatite was determined in greater detail by Beevers and McIntyre, who were able to use a more refined *X*-ray technique.[142] This confirmed the findings of Náray-Szabó, in so far as the general arrangement of the bonding was concerned. However, small changes were found to be necessary in the co-ordinates of the phosphorus atom and in some of the interatomic distances, although these alterations became of significance only if accurate values of interatomic distances were required.

The work of these authors has been confirmed by later investigations and no further structural modifications have been found to be necessary. The general arrangement of the apatite lattice was described as follows.

Along each of the three-fold axes of the structure there is a chain of calcium atoms separated from one another by a distance equal to one-half of the *c*-axis. These are bonded to their neighbours above and below by means of three shared oxygen atoms, thus forming vertical chains of alternate calcium and oxygen atoms. Each calcium is also linked to three other oxygen atoms at about the same level as its own position on the *c*-axis. This gives an arrangement which can be represented as follows:

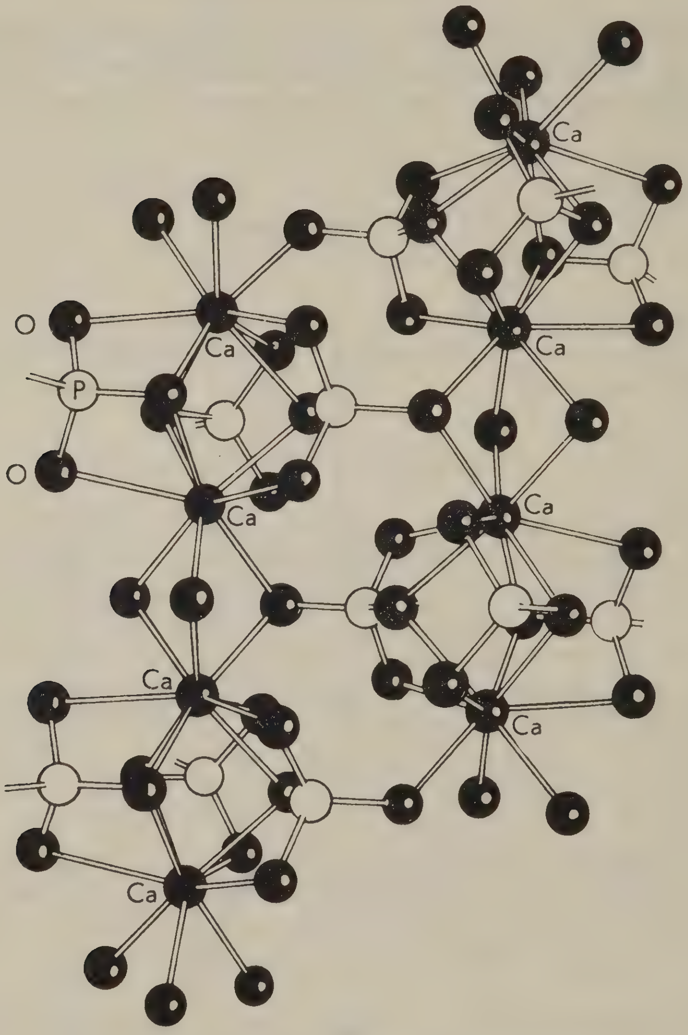


Fig. 2.—Atomic structure of fluorapatite

$$\begin{array}{ccccccccc} -\text{Ca}- & 3\text{O} & -\text{Ca}- & 3\text{O} & -\text{Ca}- \\ | & & | & & | \\ 3\text{O} & & 3\text{O} & & 3\text{O} \end{array}$$

The net effect is that every calcium atom is surrounded by nine oxygen atoms. However, because of the sharing of the oxygen atoms the calcium to oxygen ratio in the chain is 1:6.

The vertical columns of calcium and oxygen atoms are also linked to $PO_4$ groups so as to form an hexagonal network as shown in Fig. 1.

This results in a honeycomb structure having channels extending right through it in the direction of the *c*-axis. In the walls of these channels there are oxygen atoms which are so arranged as to form six recesses per unit length of each channel. Calcium atoms fit about halfway into these recesses and the fluorine atoms fit between the groups of three calcium atoms positioned at the same level. The channels and the recesses formed by the oxygen atoms are shown in Fig. 2.

In Fig. 3 the effect of inserting the calcium and fluorine atoms in the channels is seen.

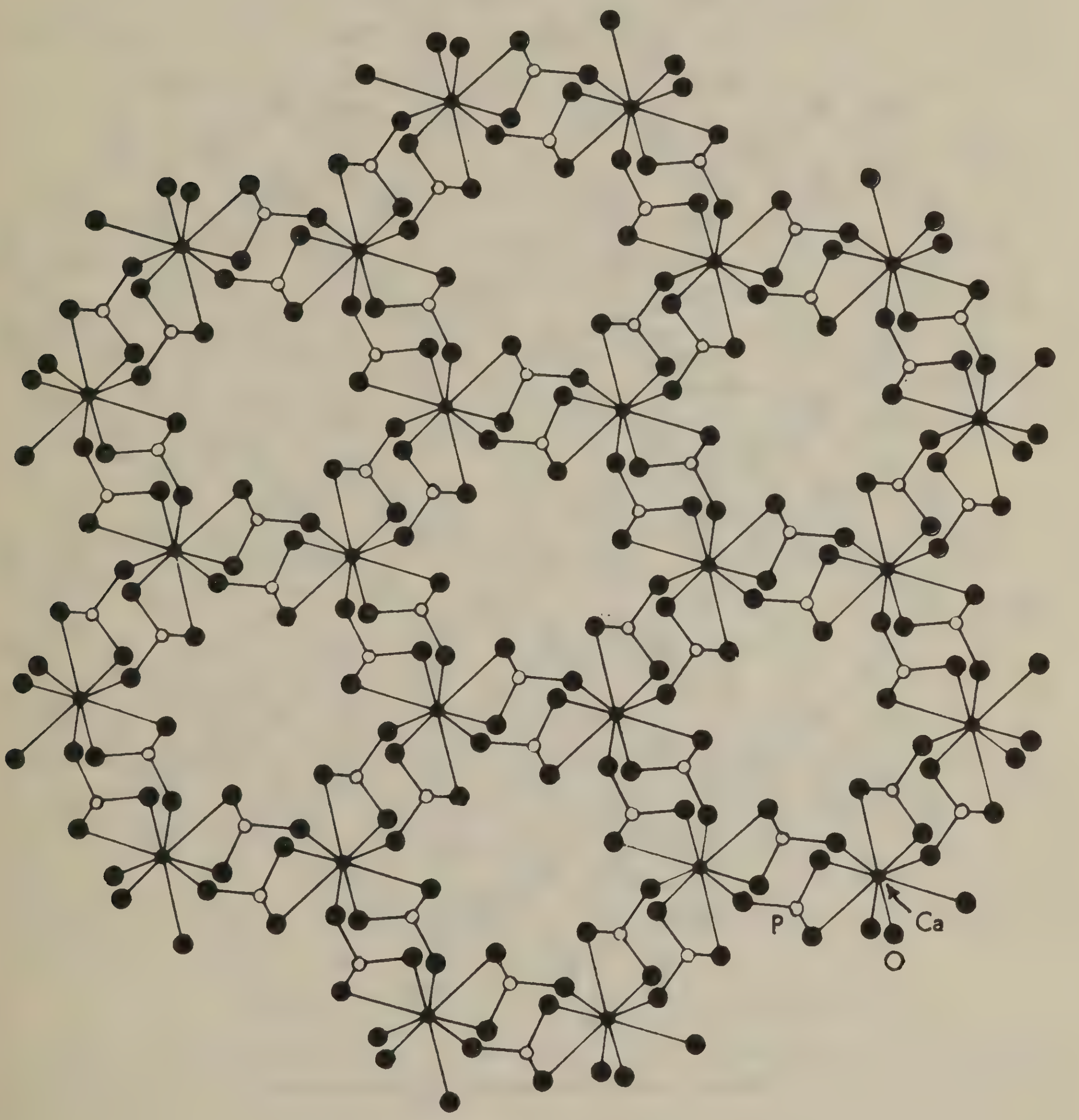


FIG. 3.—Atomic structure of fluorapatite

Fig. 4 shows the vertical columns formed by the calcium, oxygen and phosphorus atoms.

The arrangement of the calcium atoms and $PO_4$ groups gives a very stable lattice structure and determines the size of the hexagonal channels. The planar arrangement of three calcium atoms around each fluorine atom makes the whole structure very selective as regards ions which can occupy the positions of the fluoride ions. This is shown by a comparison of fluorapatite with hydroxyapatite. Since the hydroxyl ion is a little larger than the fluoride ion, the effect is to expand the hydroxyapatite structure as compared with that of fluorapatite.

These conclusions have received support[143] from more recent studies (see below) on the effect of substituting various ions in fluorapatite. Halogens do not take part in directly building up the lattice and replacement of fluorine atoms by chlorine or bromine atoms or by hydroxyl ions does not give rise to any serious alteration of the hexagonal structure. The general lattice arrangement is also still preserved, with some increase in dimensions, when strontium or barium is substituted for calcium.[144]

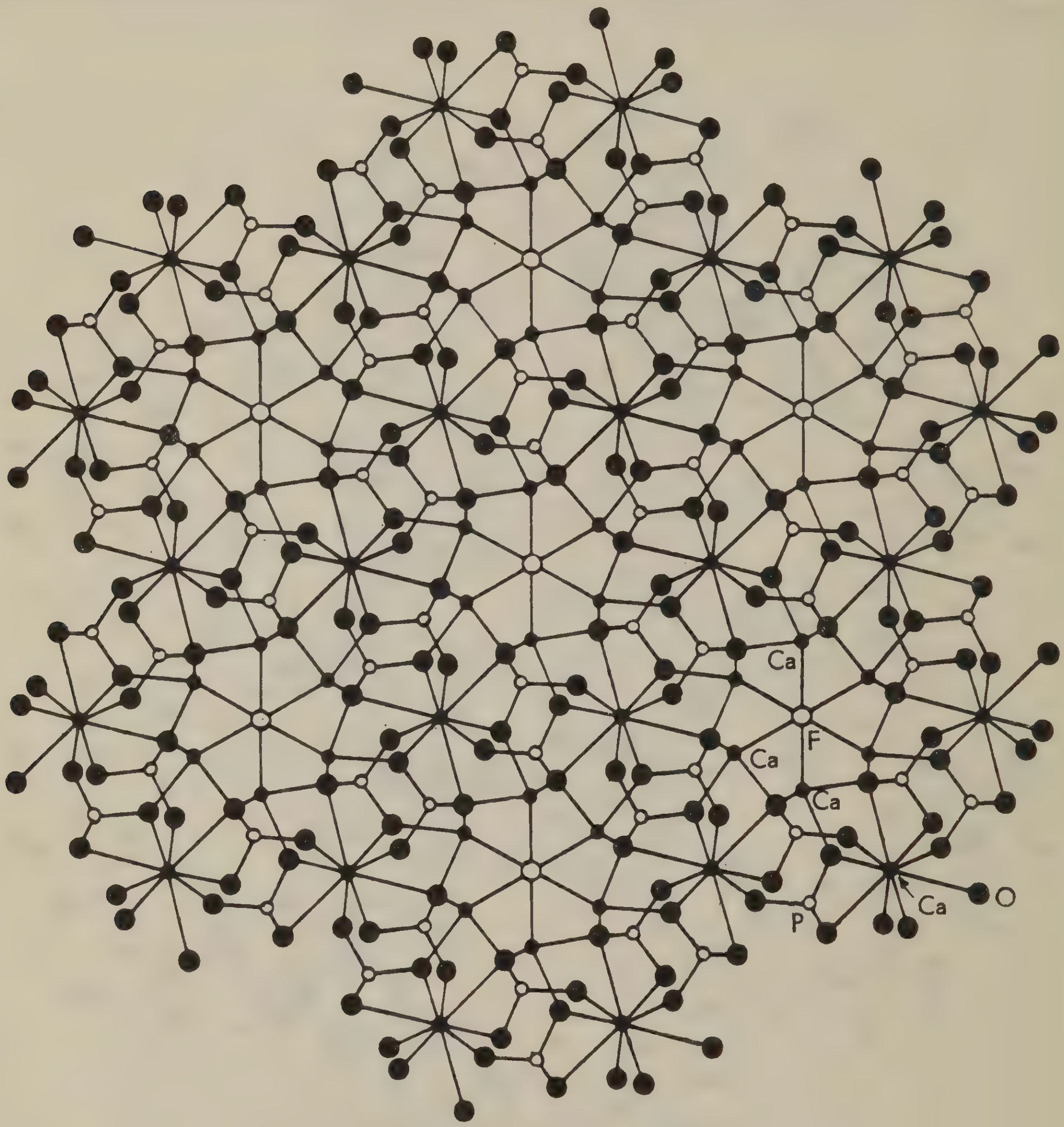


Fig. 4.—Atomic structure of fluorapatite

## Anionic Substitutions in Apatite

Fluorapatite, $Ca_{10}F_2(PO_4)_6$ or $3Ca_3(PO_4)_2,CaF_2$, is often considered to be the primary mineral from which chlorapatite and hydroxyapatite are derived by replacement of the fluorine by chlorine or hydroxyl ions. Chemically, however, fluorapatite is the most stable of the apatites and hydroxyapatite the least stable, the general direction of substitution reactions favouring the fluoride ion. Direct replacement of the fluoride ion in fluorapatite by other ions does not occur.[130] Several chlorapatite minerals are known, but the corresponding bromapatite and iodoapatite minerals have not been reported. From structural considerations it has been stated[145] that an iodoapatite is unlikely to exist. However, this possibility does not seem to have been investigated in the light of more recent knowledge of the structure of apatites.

### SUBSTITUTION BY HALOGENS

The substitution of halogens in the apatites has been studied by examining the reactions of calcium hydroxyapatite and tricalcium phosphate. Pure hydroxyapatite was prepared by saturating a solution of phosphoric acid at 100°C. to the phenolphthalein end-point, using calcium hydroxide.[146] The precipitate was dried and then calcined for a few hours at 800°C.[147] Heating hydroxyapatite with calcium chloride for 12 hr. at 800–900°C. *in vacuo* or in a dry, inert atmosphere formed chlorapatite according to the equation[148]:

$$3Ca_3(PO_4)_2{,}Ca(OH)_2 + CaCl_2 = 3Ca_3(PO_4)_2{,}CaCl_2 + CaO + H_2O$$

Under similar conditions the following reactions occurred with calcium fluoride:

$$3Ca_3(PO_4)_2{,}Ca(OH)_2 + CaF_2 = 3Ca_3(PO_4)_2{,}CaF_2 + CaO + H_2O$$
$$3Ca_3(PO_4)_2{,}CaCl_2 + CaF_2 = 3Ca_3(PO_4)_2{,}CaF_2 + CaCl_2$$

When the above reactions were carried out with insufficient calcium halide for complete conversion, mixed apatites were obtained.[149] At temperatures above 600°C. water reacted with chlorapatite to replace the chlorine atom by hydroxyl ion. It was therefore necessary to ensure rapid removal of the water formed in the first of the reactions given above. Calcium bromapatite was much more readily hydrolyzed, so that it was not possible to prepare this material by causing calcium hydroxyapatite to react with calcium bromide.[130, 143] Under these conditions fluorapatite on the other hand was stable in the presence of moisture. Hydroxyapatite was stable when heated alone at 1000°C. and lost no water, indicating that an oxyapatite does not exist as was previously thought.[139, 150]

For reactions starting with anhydrous tricalcium phosphate, this salt was prepared by heating at 900°C. an equimolecular mixture of calcium oxide and calcium pyrophosphate. The following reactions were found to occur when the reactants were heated in the solid state[130]:

$$3Ca_3(PO_4)_2 + CaX_2 = 3Ca_3(PO_4)_2{,}CaX_2$$

where X is F, Cl, Br or OH.

The formation of fluorapatite occurred easily at temperatures above 550°C. Chlorapatite was formed at temperatures above 625°C. in the absence of moisture. More rigorous precautions to exclude moisture were required to form bromapatite. The reaction between tricalcium phosphate and calcium hydroxide did not produce hydroxyapatite under dry conditions at any temperature below the decomposition point of the calcium hydroxide. In the presence of water vapour at 850°C. however, the formation of the apatite was fairly rapid, the reaction being more correctly represented by the equation:

$$3Ca_3(PO_4)_2 + CaO + H_2O = 3Ca_3(PO_4)_2{,}Ca(OH)_2$$

Under anhydrous conditions at 800–900°C. solid solutions were obtained with tricalcium phosphate and varying proportions of calcium halides, the general reaction being:

$$3Ca_3(PO_4)_2 + xCaF_2 + (1-x)CaCl_2 = 3Ca_3(PO_4)_2{,}Ca[xF_2(1-x)Cl_2]$$

Partial substitution also occurred in reactions such as:

$$3Ca_3(PO_4)_2{,}CaCl_2 + xCaF_2 = 3Ca_3(PO_4)_2{,}Ca[xF_2(1-x)Cl_2] + xCaCl_2$$

The products of the above reactions could take part in inter-diffusion processes of the type indicated below. These, however, were generally slow reactions:

$$x[3Ca_3(PO_4)_2{,}CaF_2] + (1-x)[3Ca_3(PO_4)_2{,}CaCl_2] = 3Ca_3(PO_4)_2{,}[xF_2(1-x)Cl_2]Ca$$

In all the materials obtained from the above reactions of calcium hydroxyapatite or of tricalcium phosphate the general arrangement of the apatite structure was preserved, with small changes in lattice dimensions. As fluorine was replaced by other halides or by hydroxyl ion the *a*-parameter of the unit cell increased and the *c*-parameter decreased. The variations in these parameters are shown graphically in Figs. 5 and 6.[130]

Fig. 7 shows the relationship between the lattice parameters of the calcium halogen-apatites and the ionic radii of the halogen ions.[143]

Somewhat different results were obtained[130] when halogen substitution reactions were studied using *precipitated* tricalcium phosphate as starting material. This salt was obtained by double decomposition from solutions of calcium chloride and disodium phosphate at room temperature. It had an *X*-ray diagram similar to, but not identical with, that of calcium fluorapatite, and was shown to be $3Ca_3(PO_4)_2, \frac{1}{2}H_2O$. At 625°C. dehydration occurred to form mainly anhydrous tricalcium phosphate with a little calcium hydroxyapatite. Heating at 800°C. produced a pure, anhydrous tricalcium phosphate.

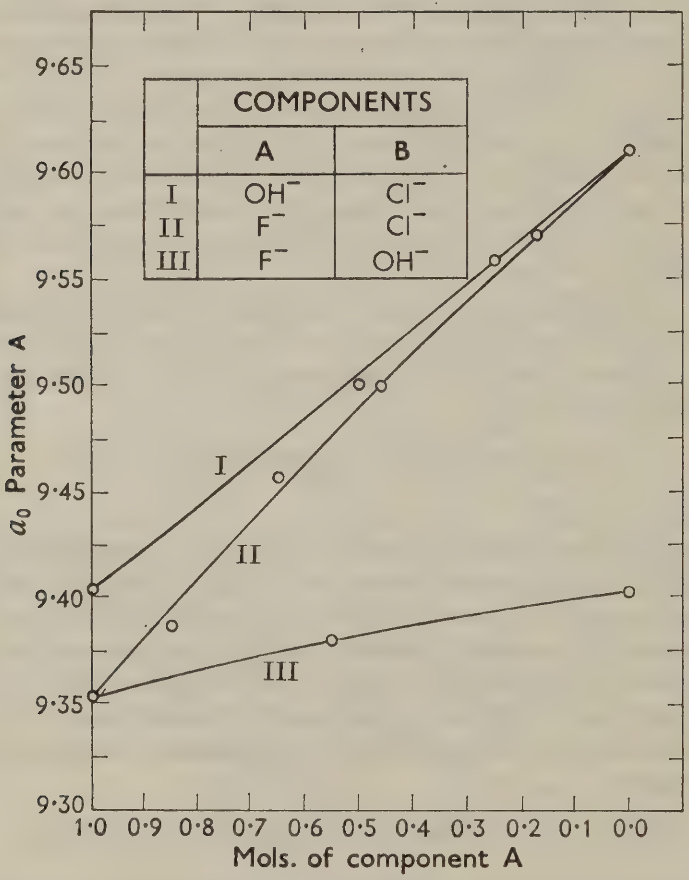


FIG. 5.—Effect of anion substitution on $a_0$-parameter of calcium apatites

Precipitated tricalcium phosphate reacted slowly with calcium fluoride at 550°C. and above to give calcium fluorapatite. With calcium chloride a mixed chlorohydroxyapatite was formed at temperatures below 625°C., but at higher temperatures a pure chlorapatite was obtained by heating the mixture rapidly over phosphorus pentoxide in a vacuum. A bromapatite was not obtained from precipitated tricalcium phosphate unless the latter was dehydrated before being mixed with calcium bromide. Heating mixtures of the phosphate and calcium hydroxide did not give a pure hydroxyapatite. At 350°C. the lime was dehydrated to calcium oxide, and above 625°C. the tricalcium phosphate lost its water. The product was mainly anhydrous tricalcium phosphate, calcium oxide and a little hydroxyapatite. By prolonged heating at 850°C. a nearly pure hydroxyapatite could be obtained in the presence of water vapour.

Precipitated tricalcium phosphate removes the fluoride from water containing calcium fluoride and in the presence of excess of the latter is slowly converted into calcium fluorapatite.[151] In the above reactions it appeared that the halogen ions entered the lattice of the calcium phosphate in preference to replacing the water of hydration. These observations were in agreement with the view[130, 152] that precipitated tricalcium phosphate is an apatite in which calcium and fluoride ions are replaced by $\frac{1}{2}H_2O$.

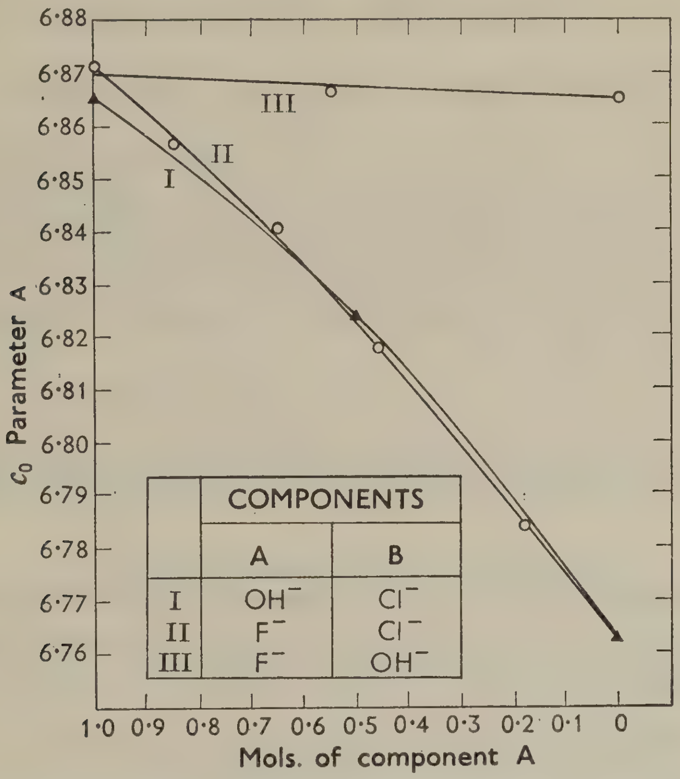


FIG. 6.—Effect of anion substitution on $c_0$-parameter of calcium apatites

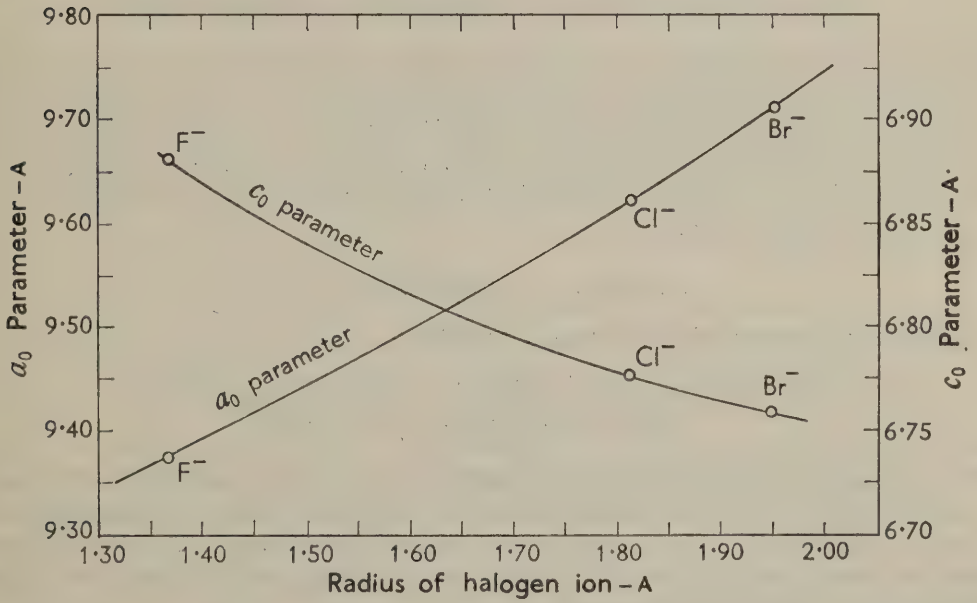


FIG. 7.—Relationship between lattice constants of calcium halogen-apatites and ionic radius of halogen ions

Other reactions involving the fluoride ion and leading to the formation of calcium fluorapatite have been studied. Although these are not anionic substitutions of the type discussed above, the reactions are of interest in showing how the fluorapatite structure can be built up from other phosphates. Calcium fluoride and calcium pyrophosphate react in the solid state at 800–1000°C. in the proportions given by the equation:

$$18Ca_2P_2O_7 + 14CaF_2 = 5[3Ca_3(PO_4)_2,CaF_2] + 6POF_3$$

The product[153] contains a small amount of calcium pyrophosphate and the weight loss is less than corresponds to the above equation. The reaction, however, is complex, and the equation agrees with the experimental results only if the reaction is carried out very rapidly, e.g. by putting small quantities into a furnace at 1000°C. At lower temperatures or with slower heating there is evidence[154] that a fluorophosphate, in which one of the oxygen atoms in a $PO_4$ group is replaced by fluorine, is formed by the reaction:

$$2Ca_2P_2O_7 + CaF_2 = Ca_3(PO_4)_2 + 2CaPO_3F$$

In the presence of calcium fluoride the fluorophosphate gives an unstable intermediate compound which then decomposes into fluorapatite and phosphorus oxyfluoride:

$$6CaPO_3F + CaF_2 = Ca_7(PO_3F)_6.F_2$$
$$3[Ca_7(PO_3F)_6,F_2] = 6POF_3 + 2[3Ca_3(PO_4)_2,CaF_2] + CaF_2$$

The main reaction can therefore be represented as the sum of four others according to the following scheme:

$$\begin{aligned} 18Ca_2P_2O_7 + 9CaF_2 &= 9Ca_3(PO_4)_2 + 18CaPO_3F \\ 18CaPO_3F + 3CaF_2 &= 3Ca_7(PO_3F)_6,F_2 \\ 3[Ca_7(PO_3F)_6,F_2] &= 6Ca_3(PO_4)_2 + 3CaF_2 + 6POF_3 \\ 15Ca_3(PO_4)_2 + 5CaF_2 &= 5[3Ca_3(PO_4)_2,CaF_2] \\ \hline 18Ca_2P_2O_7 + 14CaF_2 &= 5[3Ca_3(PO_4)_2,CaF_2] + 6POF_3 \end{aligned}$$

By using a mixture of one mole of calcium fluoride and 0·90 moles of calcium pyrophosphate and heating quickly at 800–950°C. a pure calcium fluorapatite is obtained.

At higher temperatures, e.g. above 1300°C., calcium pyrophosphate reacts with fluorapatite to form tricalcium phosphate, calcium metaphosphate and phosphorus oxyfluoride. This reaction is probably brought about by the decomposition[155] of the pyrophosphate at 1200°C.:

$$3Ca_2P_2O_7 = 2Ca_3(PO_4)_2 + P_2O_5$$

The phosphorus pentoxide then reacts as follows:

$$3[3Ca_3(PO_4)_2,CaF_2] + 22P_2O_5 = 30Ca(PO_3)_2 + 2POF_3$$
$$Ca_3(PO_4)_2 + 2P_2O_5 = 3Ca(PO_3)_2$$

The corresponding reaction between calcium fluoride and calcium metaphosphate is equally complex and is markedly affected by the molar ratio of the reactants. Rapid heating at 800–900°C. of a mixture of 4 moles of fluoride and 3 moles of metaphosphate gives calcium fluorapatite as the final solid product. This agrees approximately with the overall equation:

$$9Ca(PO_3)_2 + 11CaF_2 = 2[3Ca_3(PO_4)_2,CaF_2] + 6POF_3$$

On the other hand calcium metaphosphate and fluorapatite react at temperatures above 600°C. giving calcium pyrophosphate as the end-product.[156] At 1000°C. this reaction is represented by the equation:

$$3[3Ca_3(PO_4)_2,CaF_2] + 14Ca(PO_3)_2 = 22Ca_2P_2O_7 + 2POF_3$$

It appears therefore that the reaction between calcium fluoride and metaphosphate can best be represented as taking place in the following stages[154]:

$$\begin{aligned} 5Ca(PO_3)_2+3CaF_2 &= 4Ca_2P_2O_7+2POF_3 \\ 6Ca_2P_2O_7+3CaF_2 &= 5Ca_3(PO_4)_2+2POF_3 \\ 3Ca_3(PO_4)_2+CaF_2 &= 3Ca_3(PO_4)_2,CaF_2 \end{aligned}$$

Reviews[157-9] and summaries[160, 161] of the reactions discussed above and of related subjects[130, 143, 162-3] have been made by a number of authors.

### SUBSTITUTION BY HYDROXYL IONS

After fluorine, the hydroxyl ion is the anion which is most commonly found in the apatite minerals and phosphorites. From a purely chemical point of view the hydroxyl ion may be regarded as taking the place of the fluoride ion in calcium fluorapatite. This view, however, does not explain some of the observations and conclusions resulting from crystallographic and *X*-ray investigations into the structure of apatites. Although it is now known that the hydroxyl ion can occupy the same position in the lattice as halide ions, and that pure specimens of hydroxyapatite can be made,[125, 126, 129, 130] it is still necessary to explain the variable composition found in the naturally occurring mineral. Many views and explanations, some of which are discussed below, have been put forward to account for the behaviour of the hydroxyl ion.

Some of the earlier attempts (Mellor, III, 901–5) at explaining the variation in the composition of hydroxyapatite considered the latter as being composed of tricalcium phosphate and basic calcium phosphates. This view, however, did not agree with the results later obtained by *X*-ray methods of examination. In particular, it was found that hydroxyapatites having different chemical compositions gave the same type of *X*-ray diffraction pattern. It was also observed that compounds which gave almost identical *X*-ray powder diagrams could have a molar calcium to phosphorus ratio which varied between 4/3 and 2. These facts were at first explained by assuming that calcium or phosphate ions were adsorbed on the surface of the apatite in amounts required to bring the calcium to phosphorus ratio to the observed value.[164-5] However, as Van Wazer[166] (p. 536) has pointed out, for a material having a calcium to phosphorus ratio of 1·5 this hypothesis requires an abnormally thick adsorption layer on the crystal surface. In addition, experiment has shown that apatites having a low ratio do not lose phosphate ions when heated with water.[167] Similar results have been obtained in hydrothermal bomb experiments on the crystal growth of hydroxyapatite at 300°C. and pressures up to 2000 lb. per sq. in.[168] The use of radioactive isotopes to study exchange reactions in calcium phosphates has shown that the rate of exchange of both calcium and phosphorus is the same irrespective of the calcium to phosphorus ratio of the material.[169-73]

An alternative suggestion has been put forward[174-5] according to which actual substitution rather than adsorption[176] of ions occurs on the crystal surface. According to Van Wazer[166] (p. 537) calculation shows that this hypothesis would account for the existence of hydroxyapatites having a calcium to phosphorus ratio between 1·4 and 1·8 if isomorphic substitution of hydronium for calcium ions also takes place.

It has also been postulated[177] that isomorphic substitution throughout the crystal lattice could occur, as distinct from only surface phenomena. In this view it was supposed that calcium is replaced by hydrogen ions and water. Although the idea was explained in some detail, it does not seem to have been developed to any extent.

The fact that the same *X*-ray diffraction pattern was obtained from hydroxyapatites of different compositions has been accounted for by assuming the existence of a defect apatite structure.[178] According to this view calcium atoms are missing from certain positions in the apatite lattice, electrical neutrality being preserved by the addition of hydrogen ions. It was thought[179] that this would explain the structure of the mineral whitlockite, $Ca_3(PO_4)_2$. On the other hand, the concept of a defect apatite lattice has been rejected as misleading. It was emphasized that any interpretation of the structure of either the hydroxyapatites or the carbonate-apatites must take into account the amounts of water and carbon dioxide present.[180] These were important because of isomorphic substitutions which can occur and which involve the following ionic replacements:

$$PO_4^{3-} \rightarrow 4OH^-, \quad 3PO_4^{3-} \rightarrow 4CO_3^{2-}, \quad Ca^{2+} \rightarrow H_3O^+$$

The problem of the structure and composition of hydroxyapatite has been investigated by examining precipitated calcium phosphates, compounds derived from melts, and by the study of the solid state reactions already discussed. On occasion apparently conflicting evidence has been obtained because of the failure to recognize the anomalous behaviour of the phosphates.

In the case of the precipitated phosphates it has been suggested[181] that many contradictions could be resolved by taking into account the following considerations:

Between the CaO and $CaHPO_4$ phases of the ternary system $CaO–P_2O_5–H_2O$, there exists a series of solid solutions which have an apatite structure. Hydroxyapatite and tricalcium phosphate do not always exist in aqueous solution as unique stoicheiometric compounds. In addition the apatite structure is very stable, but permits a number of unusual types of substitution which involve considerable numbers of ions. The last point was originally made by McConnell,[182] who showed that although hydroxyapatite could be formulated as $3Ca_3(PO_4)_2,Ca(OH)_2$, from a structural point of view this could not represent a definite compound with a unique composition.

In the study of phosphate melts it has been emphasized that traces of moisture can give rise to unsuspected complications, and the necessity for the rigorous exclusion of water from the system has been stressed.[181] Hydroxyapatite has been shown to be formed from binary mixtures of CaO and $P_2O_5$ at temperatures as high as 1050°C. if moisture is present.[183] Calcium phosphate and apatite melts lose all their water only at temperatures of 1400–1500°C.[184] The fact that apparently contradictory conclusions could arise through neglecting reactions caused by the presence of water has been more recently emphasized with reference to investigations into the stoicheiometry of hydroxyapatite.[185]

### OXYAPATITES

The question as to the existence of an oxyapatite was a problem which at one time engaged the attention of a number of investigators. Such a compound, in which the fluorine was supposed to be replaced by oxygen, appears to have been postulated originally to account for the variation in composition of hydroxyapatite and various precipitated phosphates (Mellor, III, 903). However, from a study of the behaviour of calcium phosphates in precipitation reactions[186–7] and an examination of phase relations in aqueous systems,[188] no evidence was found to support the existence of an oxyapatite. The phase diagrams of calcium phosphate melts also failed to indicate an oxyapatite as a solid phase.[183] From a crystallographic point of view and from a study of the substitution of silicate and sulphate groups in apatite minerals it has been concluded that an oxyapatite is unlikely to exist because an oxygen atom could not replace two hydroxyl groups in the lattice of hydroxyapatite.[189] Van Wazer[166] (pp. 510–30) reviewed the literature and from a discussion in some detail of the aqueous and the melt phase diagrams of calcium phosphates considered that there was no reason to assume that an oxyapatite existed.

Although the evidence is against the possibility of there being an oxyapatite in which the fluorine in fluorapatite is replaced by oxygen only, it appears that oxygen atoms can be accommodated in the apatite lattice when carbonate ions are present. An investigation of the structure of naturally occurring apatites resulted in the conclusion that the mineral dahllite, which may be formulated as $10CaO,3P_2O_5,CO_2,xH_2O$, is a carbonate oxyapatite.[190]

### CARBONATE APATITES

The carbonate ion is found associated with a number of phosphorus minerals and is also involved in the formation of bones, teeth and calcified tissues. The nature of the relationship between the apatite lattice and the carbonate ion has therefore been studied from the biological, chemical and mineralogical viewpoints. These investigations have resulted in many explanations and hypotheses regarding the structure of the carbonate-apatites, the conclusions reached often being very conflicting.

In the early views of the subject (Mellor, III, 896–904) it was supposed that the carbonate-apatites were mixtures or double compounds of calcium carbonate and calcium hydroxyapatite[191] or fluorapatite.[192] *X*-Ray diagrams, however, showed no diffraction lines supporting the presence of crystalline calcium carbonate. As an alternative it was suggested that the carbonate ion took the place of hydroxyl or fluoride ions[26] in the lattice.[141] On the other hand, this type of substitution did not agree with the results of *X*-ray structural investigations of the minerals. The latter work showed that the carbonate ion could not enter into the apatite structure in the same way as other anions,[193] at least so far as calcium fluorapatite was concerned.

In later investigations the problem was approached in two ways and this has given rise to two main explanations to account for the presence of carbonate in phosphorus minerals. One line of approach was concerned with the structure and biological nature of bones and teeth.[175] From a study of the surface chemistry of bone the idea emerged that carbonate ions were adsorbed on the bone surface by a process which involved an exchange of phosphate for carbonate ions.[169, 174, 194–5] Bicarbonate ions were found[196] to penetrate the hydration shell[197] of the apatite crystals in bone and to displace phosphate ions from the crystal surface. This could account for the relatively large amounts of carbonate found in bone, and the exchange reaction appeared to be the more important part of the mechanism of bone formation. Although it is generally assumed that the carbon dioxide occurs in bone as carbonate, there is fragmentary evidence that at least some of it is present as bicarbonate.[176]

The above hypothesis was supported by the fact that infra-red examination of carbonate-apatite minerals showed absorption bands due to calcite. In addition, most of the carbon dioxide could be removed by treatment of the minerals with acid, without any change in the *X*-ray pattern.[198] It was also found that synthetic apatites could take up carbon dioxide from solutions, the amount adsorbed being proportional to the carbon dioxide:phosphorus pentoxide ratio in the solution.[196] In a similar manner tricalcium phosphate can adsorb water[199] or remove calcium ions from solution.[200]

Although the adsorption theory explains many of the observations made on the nature and composition of bone material and can in part be used to account for the structure of naturally occurring carbonate-apatites, a too liberal interpretation of the theory can lead to erroneous conclusions. It has been pointed out[201] that in attempts to relate the structure and composition of the apatite in calcified tissues to those of the mineral carbonate-apatites, the following considerations must be taken into account. The nature of the apatite in bone is difficult to establish because of its small particle size. This applies less to tooth enamel which has a larger particle size, but in both instances surface phenomena are important. Because the interruption of the arrangement of atoms at the surface of a crystal results in free charges being available, the surface can bind ions from an aqueous phase. In bone the crystals are generally in contact with a constant ionic medium and this accounts for the constancy in the composition of bone salts. Surface exchange of ions is rapid, but penetration of ions into the interior of the lattice is slow and occurs only with ions capable of isomorphic substitution. There is also a close relationship between the mineral crystallites and the organic collagen fibres in bone,[202] in which the crystal growth of the apatite present may be affected.[203] Chemical analysis of bone mineral can be rendered inaccurate because of the impossibility of removing the organic component without changing the composition of the inorganic constituent. For example, in the standard procedure for removing organic material by boiling with a solution of potassium hydroxide in anhydrous glycerol, any hydrated tricalcium phosphate present in the bone will be almost completely converted to hydroxyapatite. It is therefore necessary to consider the conclusions drawn from an investigation in conjunction with actual experimental conditions.

**Refs. p. 60**

The second approach referred to above has been concerned mainly with chemical and mineralogical studies of bones, teeth and phosphorus minerals, including synthetic apatites. Early chemical analysis showed that the inorganic constituent of bones and teeth was apatite,[204] and the apatite structure was later confirmed by *X*-ray diffraction methods.[205] The composition of the apatite has been discussed on the basis of its being carbonate hydroxyapatite, hydrated tricalcium phosphate or hydroxyapatite.[206] An early conclusion, derived from a consideration of many analyses, was that bone was substantially a carbonate-apatite to which the formula $3Ca_3(PO_4)_2,CaCO_3$ was given.[207] Attention was drawn to the similarity of this to the carbonate-hydroxyapatite mineral dahllite.[208] It was later suggested[209] that the carbonate content of bone might be accounted for by considering it to be present as a separate phase in the form of calcium carbonate. The amount of calcium remaining was taken to be present in the apatite itself and this gave a calcium to phosphorus ratio near to that of hydrated tricalcium phosphate.[210] Similarities in *X*-ray patterns of bone and hydrated tricalcium phosphate[211] were put forward in support of the idea, but this had little significance because most poorly crystalline apatite precipitates give almost identical *X*-ray patterns. There is also very little evidence that calcium carbonate is present as a separate phase. Similarities in the refractive indices of bone salts and mixtures of calcium carbonate and hydrated tricalcium phosphate have also been noted.[212]

An alternative suggestion was that bone consists of hydroxyapatite and a separate phase of calcium carbonate.[213] It is well established[174-5] that although the mineral phase of bone is not simply hydroxyapatite, the latter is the major constituent.[165] The assumption of calcium carbonate as a separate phase is, however, less easy to justify, particularly in view of the effects of surface phenomena referred to above.[214] The presence of carbonate in the bone structure must therefore be accounted for in some other way. Many of the investigations concerned with this problem were connected with studies of carbonate-apatite minerals, especially francolite.[215] This mineral contains, in addition to phosphate, variable proportions of fluoride, hydroxyl and carbonate ions.[216] Its composition[217] and structure are intermediate between those of fluorapatite and the carbonate-apatite dahllite.[190]

The designation carbonate-apatite, following the original suggestion,[182] is generally applied to mineral apatites containing 2–5% of carbon dioxide. Only two varieties of this type of apatite are at present known. One of these, francolite, is a carbonate fluorapatite which contains 2–6% of fluorine and was formerly known as staffelite or grodnolite. The other, dahllite, is a carbonate hydroxyapatite, previously known as podolite, which contains less than 1% of fluorine. Investigations of the structure of these minerals have largely been concerned with the question as to whether the carbonate-apatites consist of a single phase with the carbonate as part of the lattice or a heterogeneous system consisting of micro-crystalline apatite with the carbonate as a separate phase. The earlier chemical, *X*-ray and structural data[193] showed that the carbonate ion could not replace fluorine in apatites, so that francolite was not represented by the formula $3Ca_3(PO_4)_2,CaCO_3$. From geometrical considerations[218, 193] it appeared to be very doubtful whether there was room for the carbonate ion in other positions in the lattice. Gruner and McConnell therefore suggested that carbon could replace phosphorus in the tetrahedral phosphate groups. Carbon could also replace calcium in certain positions in the lattice and fluorine and hydroxyl groups could replace some of the oxygen atoms. On this basis the formula for the apatites became $[Ca(F,Cl,OH)](Ca,C)_4[(P,C)(O,OH,F)_4]_3$ and francolite was represented as being[182] $(Ca_3,F)_2(P,C)_6(O,OH,F)_{24}(Ca,C)_4$. Investigations on a number of samples of francolite[219, 220] showed that they could all be interpreted in terms of this structure. A sample from New Zealand was shown[217] to have the formula

$$(Ca,Na,K,C)_{10}(P,C,Si,Al)_6(OH,F)_{3\cdot3}O_{22\cdot7}$$

In one from the coal measures carbon was thought to enter the lattice in some of the calcium and phosphorus positions and not to be present as carbonate.[216] A later and more accurate chemical and *X*-ray analysis gave a structure in which there was isomorphous substitution of carbon for phosphorus, water for calcium atoms and $(OH)_4$ groups for phosphate. Taking into account some replacement of calcium by magnesium and strontium as well as the presence of small quantities of sodium, the formula proposed[221] was

$$[(Ca,Mg,Sr)_{9\cdot89}Na_{0\cdot01}(H_2O)_{0\cdot1}]F_2[P_{5\cdot36}(\tfrac{4}{3}C)_{0\cdot51}(4H)_{0\cdot13}]O_{23\cdot88}F_{0\cdot12}$$

The above types of structure were suggested for the apatite in calcified tissues,[222] attention being drawn to the close relationship between the nature of the carbonate in bone and tooth minerals and that in the natural carbonate-apatites.[223] The structure proposed for dentin and enamel of teeth was $(OH)_2Ca_6[(P,C)O_4]_6(Ca,C)_4$. This indicated that all the calcium ions were united to the $PO_4$ groups and that the hydroxyl groups were in contact with six calcium atoms only and were separated from the phosphate groups. Carbon replaced a number of calcium and phosphorus atoms, with the restriction that only the calcium atoms on the internal threefold axes could be replaced by carbon. More recently it has been concluded that dental enamel is a carbonate-hydroxyapatite similar to dahllite.[224]

The structures proposed for francolite have been criticized both on account of the unusual types of substitution proposed and also because of the $CO_4$ group. An alternative structure in which carbon could replace phosphorus but not calcium was proposed. This postulated the molecule $3CaCO_3,Ca(F,OH)_2$ in which the carbon was present as carbonate, the formula of francolite being supposed[225] to be

$$Ca_5C_3O_9(F,OH)_4$$

The other opinion, viz., that the carbonate in the carbonate-apatites is present as a separate phase, has been supported by the fact that the carbonate ion is too large to fit into the apatite lattice.[218] Since crystalline calcium carbonate has not been detected by *X*-ray diffraction it is assumed that the carbonate is present in an amorphous form. On the other hand, only with very refined techniques would it be possible to detect by this means crystalline carbonate in the amounts (2–5%) usually present in carbonate-apatites. Carlström reviewed the evidence and favoured the existence of a separate carbonate phase.[201] McConnell,[226] however, considered that there was insufficient evidence to support this conclusion. A study of the $Na_3PO_4$–$CaCO_3$–$H_2O$ system at low temperatures, in which carbonate-apatites of variable composition were obtained, supported the view that carbonate could be entirely present in the apatite lattice.[227] It has also been claimed[228] that a carbonate-apatite can be prepared by heating a suspension of calcium carbonate in monopotassium phosphate solution at 90°C. From an infra-red examination it was concluded that hydroxyl had been replaced by carbonate ions. This was criticized on the basis of insufficient data and the use of concepts which had been shown not to be valid.[229] Independent examination showed that the reference specimen used for the infra-red spectrum examination was a mixture of calcium carbonate and calcium hydroxyapatite.[196] It also contained water and had not been ignited, and allowing for this the conclusion was that carbonate did not replace hydroxyl ion. Hydrothermal bomb experiments, in which the amorphous form of calcium hydroxyapatite was heated with solutions of sodium carbonate or sodium bicarbonate at 400°C., showed that although the carbonate ion disturbed the arrangement of the lattice, it did not enter it.[230]

More recent work has been concerned with attempts to prepare carbonate-apatites by solid-state reactions.[231] Calcium carbonate and tricalcium phosphate do not react at temperatures below 700°C., and above this the carbonate dissociates to give a mixture of phosphate and calcium oxide, no apatite being obtained. Under extremely dry conditions no further reaction occurs on heating to 900°C., but if traces of atmospheric moisture are present, some hydroxyapatite is formed according to the equation:

$$3Ca_3(PO_4)_2 + CaO + H_2O = 3Ca_3(PO_4)_2,Ca(OH)_2$$

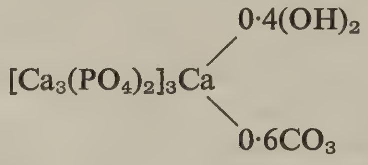
When heated at 850–900°C. in the presence of dry carbon dioxide, about half of the phosphate is converted to carbonate-apatite in 8 days. At 1000°C. in a closed vessel and in the presence of carbon dioxide at 10–20 atm. pressure, a 30% yield of apatite is obtained in 120 hr., according to the equation:

$$3Ca_3(PO_4)_2 + CaCO_3 = 3Ca_3(PO_4)_2,CaCO_3$$

By heating calcium hydroxyapatite for 48 hr. in a stream of carbon dioxide at 850–950°C., approximately 60% of the hydroxyl groups were replaced according to the reaction:

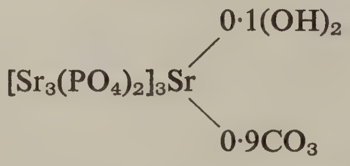
$$3Ca_3(PO_4)_2,Ca(OH)_2 + CO_2 = 3Ca_3(PO_4)_2,CaCO_3 + H_2O$$

The product was considered to be a solid solution of hydroxyapatite and carbonate-apatite and was represented by the formula:



$$[Ca_3(PO_4)_2]_3Ca\begin{matrix} / \, 0{\cdot}4(OH)_2 \\ \backslash \, 0{\cdot}6CO_3 \end{matrix}$$

The reaction of carbon dioxide with hydroxyapatite at 900–950°C. under dry conditions has been applied to the corresponding strontium and barium compounds The replacement of calcium in the apatite structure by strontium and barium causes a progressive increase in the lattice dimensions. Consequently it is possible to replace 90% of the hydroxyl groups in strontium hydroxyapatite,[232] to give a material formulated as:



$$[Sr_3(PO_4)_2]_3Sr\begin{matrix} / \, 0{\cdot}1(OH)_2 \\ \backslash \, 0{\cdot}9CO_3 \end{matrix}$$

With barium hydroxyapatite[233] complete replacement of hydroxyl occurs to give barium carbonate apatite, $3Ba_3(PO_4)_2,BaCO_3$.

These investigations showed that partial or complete replacement of two hydroxyl ions by one carbonate ion can take place in the alkaline earth hydroxyapatites. It was concluded[143] therefore that the carbonate ion can occupy the same positions in the apatite lattice as the halogen ions. This is in disagreement with the earlier conclusions[193] resulting from *X*-ray and crystallographic studies on calcium apatites. Three hypotheses have thus been put forward to account for the structure of the carbonate-apatites. There does not seem to be conclusive evidence with which to support any one of them completely.

### SUBSTITUTION OF THE $PO_4$ GROUP

In addition to the replacement of the fluorine in fluorapatite by mono-valent ions, substitution by a number of polyvalent ions can occur. This type of substitution, however, takes place in the phosphate groups. Arsenic as $AsO_4^{3-}$ ion replaces phosphorus in minerals such as fermorite, $(Ca,Sr)_{10}(PO_4,AsO_4)_6.F,OH$,[234] and svabite, $(CaPb)_{10}(PO_4,AsO_4)_6.F,OH$.[235] This substitution is more common in the pyromorphite series, giving rise to mimetite, $Pb_{10}(AsO_4,PO_4)_6Cl_2$, in which nearly all of the phosphorus may be replaced by arsenic.

Phosphate ions are also replaced by silicate and sulphate. In ellestadite,[189] $Ca_{10}(PO_4,SO_4,SiO_4)_6.F,Cl,OH,CO_3$, for example, half of the phosphate is replaced by these two ions. A similar replacement occurs in wilkeite,[236]

$$Ca_{10}(PO_4,SO_4,SiO_4)_6F,OH$$

This mineral has been prepared by sintering at 1200°C. a stoicheiometric mixture of tricalcium phosphate, calcium orthosilicate, $Ca_2SiO_4$, calcium sulphate and calcium fluoride.[237] The apatite structure is still retained when all of the phosphate has been replaced by sulphate.[238–9]

As will be seen from Table XV (p. 39) there are other phosphorus minerals in which phosphate is replaced by vanadate, uranyl, borate and chromate ions.

### Cationic Substitutions in Apatite

A number of artificial apatites containing various combinations of cations have been prepared, and are of interest in connection with the structure and general behaviour of the apatite lattice.

Strontium hydroxyapatite has been made by hydrolyzing tristrontium phosphate with 0·10N. sodium hydroxide solution, by precipitating strontium-containing solutions with alkali phosphates or by heating a stoicheiometric mixture of tristrontium phosphate and strontium carbonate in hydrogen at 1150°C.[240] It has also been prepared by neutralizing phosphoric acid solution with strontium hydroxide (to phenolphthalein) in the cold and then boiling the mixture.[143] Addition of excess of potassium dihydrogen phosphate solution to one of strontium chloride yields strontium hydroxyapatite if the mixture is maintained at pH 10–14 by adding potassium hydroxide. With excess of strontium chloride some strontium chlorapatite is also formed under these conditions. In more acid solutions (pH 6–10) mixtures of strontium hydroxyapatite and distrontium phosphate are obtained.[241] A hydrothermal synthesis from strontium phosphate and strontium hydroxide in 2N. sodium hydroxide solution at 420°C. has been described.[242]

A hydrated tristrontium phosphate, $3Sr_3(PO_4)_2,\frac{1}{2}H_2O$, which has an apatite structure similar to that of the calcium compound, has been prepared by causing disodium phosphate and strontium chloride solutions to react under ammoniacal conditions at pH 9·5 and at room temperature according to the equation[243, 143]:

$$6Na_2HPO_4+9SrCl_2+6NH_4OH = 3Sr_3(PO_4)_2,\tfrac{1}{2}H_2O+6NH_4Cl+12NaCl+5\tfrac{1}{2}H_2O$$

After being washed, the precipitate is dried at 90°C. The product loses its water of hydration between 650° and 850°C.

Strontium fluorapatite is formed when solid strontium hydroxyapatite is caused to react with strontium fluoride at 600–1050°C., the reaction being:

$$3Sr_3(PO_4)_2,Sr(OH)_2+SrF_2 = 3Sr_3(PO_4)_2,SrF_2+SrO+H_2O$$

Fluorapatite is also obtained by solid state reaction of strontium fluoride with anhydrous tristrontium phosphate at 550°C. or with the hydrate at 1000°C.[244] Under anhydrous conditions, strontium fluorapatite has been prepared by heating strontium mono-fluorophosphate mono-hydrate. The latter dehydrates at 150°C. and between 450° and 550°C. is transformed into strontium pyrophosphate, with volatilization of phosphorus oxyfluoride:

$$5SrPO_3F = 2Sr_2P_2O_7+SrF_2+POF_3$$

At 800°C. the pyrophosphate and strontium fluoride react to form strontium fluorapatite and phosphorus oxyfluoride:

$$18Sr_2P_2O_7+14SrF_2 = 5[3Sr_3(PO_4)_2,SrF_2]+6POF_3$$

In the presence of moisture and at temperatures above 450°C., no apatite is obtained, the products being strontium pyrophosphate and hydrogen fluoride[245]:

$$2SrPO_3F+H_2O = Sr_2P_2O_7+2HF$$

Strontium chlorapatite and bromapatite are made by heating tristrontium phosphate with strontium chloride or bromide for 2 hr. at 900°C. in a stream of dry nitrogen.[143]

Solid solutions of the strontium halo-apatites have been obtained by heating at 1000°C. mixtures in varying proportions of the individual halo-apatites. The effect of changing the halogen ion on the lattice constants is shown in Figs. 8 and 9 where the constants for the pure apatites are plotted against the radius of the halogen ion.[143]

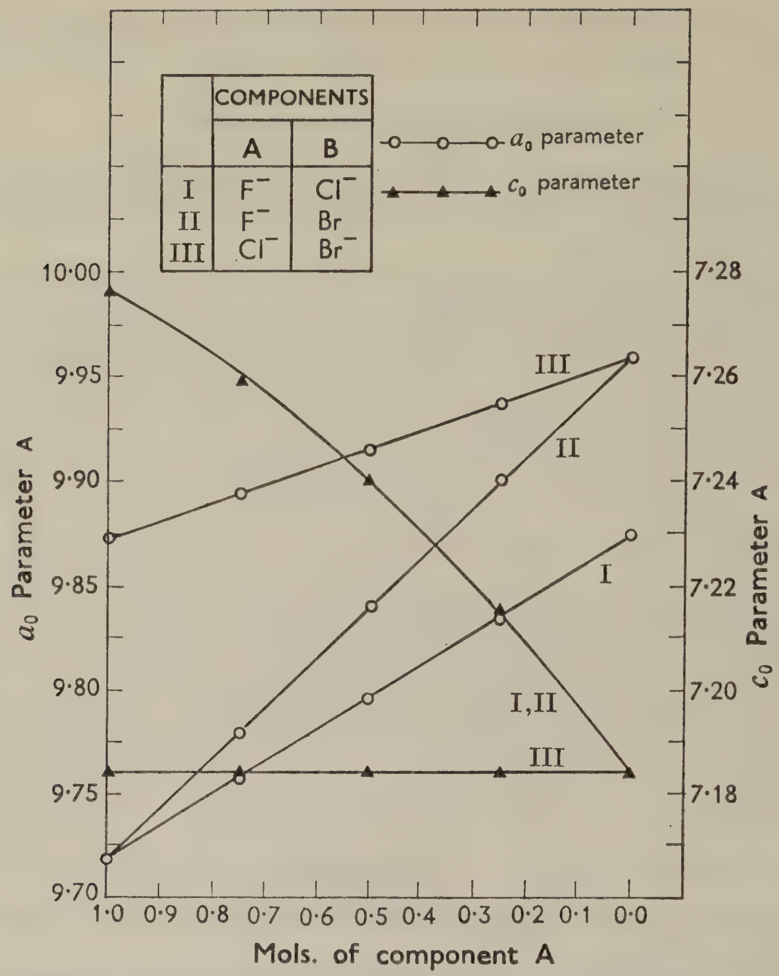


FIG. 8.—Effect of halogen substitution on lattice constants of strontium apatites

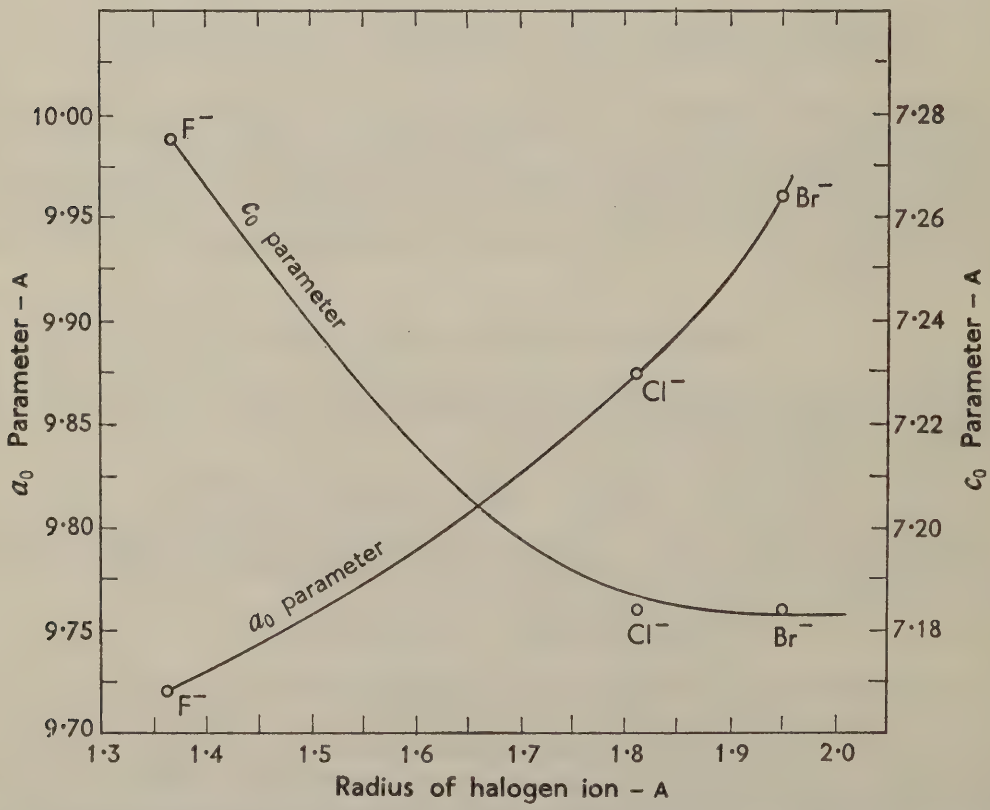


FIG. 9.—Relationship between lattice constants of strontium halogen-apatites and ionic radius of halogen ion

Barium hydroxyapatite cannot be prepared by precipitation from aqueous solutions in the same way as calcium and strontium hydroxyapatites. The latter form the most stable phase in boiling solutions, whereas for barium the most stable compound is tribarium phosphate. Neutralization of phosphoric acid with barium hydroxide in the manner described previously for strontium, does not therefore lead to a pure barium hydroxyapatite as the product is invariably heavily contaminated with tribarium phosphate. The latter does not have an apatite structure and it is interesting to note that a hydrate corresponding to $3Ba_3(PO_4)_2,\frac{1}{2}H_2O$ cannot be prepared.[246] Pure barium hydroxyapatite is formed, however, when barium hydroxide solution is only partly neutralized with phosphoric acid.[247] In the preparation from barium chloride solution and monopotassium phosphate, barium hydroxyapatite is formed only in the presence of excess of barium chloride and in solutions at least 3M. in chloride ion. The solution must be kept at pH 10 by addition of potassium hydroxide.[241] Barium hydroxyapatite has also been synthesized by heating tribarium phosphate with barium peroxide for 6 hr. at 1000°C. in an atmosphere of water vapour.[248] The reaction is:

$$3Ba_3(PO_4)_2 + BaO_2 + H_2O = 3Ba_3(PO_4)_2,Ba(OH)_2 + \frac{1}{2}O_2$$

Barium fluorapatite, chlorapatite and bromapatite have been made by heating stoicheiometric mixtures of anhydrous tribarium phosphate and the appropriate barium halide at 600–900°C. The lattice constants of these materials are shown in Fig. 10.

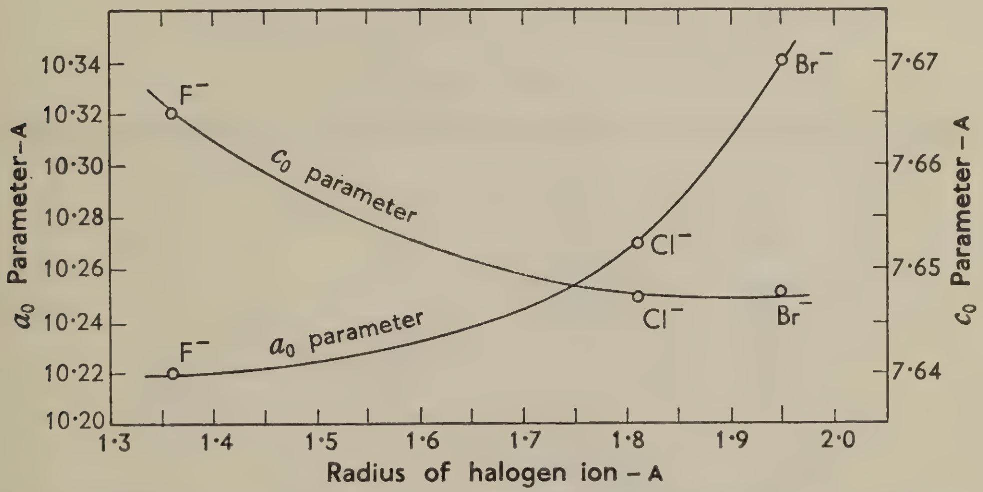


FIG. 10.—Variation in lattice constants of barium halogen apatites with ionic radius of halogen ion

These three apatites are miscible in all proportions and form solid solutions in the same way as the calcium and strontium compounds. The lattice constants vary linearly with the composition of the solid solution.[143]

The formation of solid solutions of apatites containing the same halogen but two different alkaline-earth cations has also been studied.[249] The solutions were prepared by heating together known quantities of the pure components for 3 hr. at 1000°C. The products were then submitted to *X*-ray examination. The calcium and strontium apatites and the strontium and barium apatites were found to be miscible in all proportions. The lattice constants were a linear function of the composition of the solid solutions as shown in Figs. 11 and 12. On the other hand complete miscibility was not observed with calcium and barium apatites. For the fluorapatites the region of non-miscibility extended from 6 to 64 atom-% of barium. Outside this range the $a_0$-parameter was linearly related to the composition, the same function applying to areas on both sides of the two-phase zone. For the $c_0$-parameter, however, two linear functions are required to relate parameter and composition. These observations are shown for the fluorapatites in Fig. 13. Similar results were found for the mixed calcium–barium chlorapatites and the corresponding bromapatites. The region of non-miscibility lay between 8 and 61 atom-% of barium in both instances.

Solid solutions of calcium and strontium hydroxyapatites have been prepared by

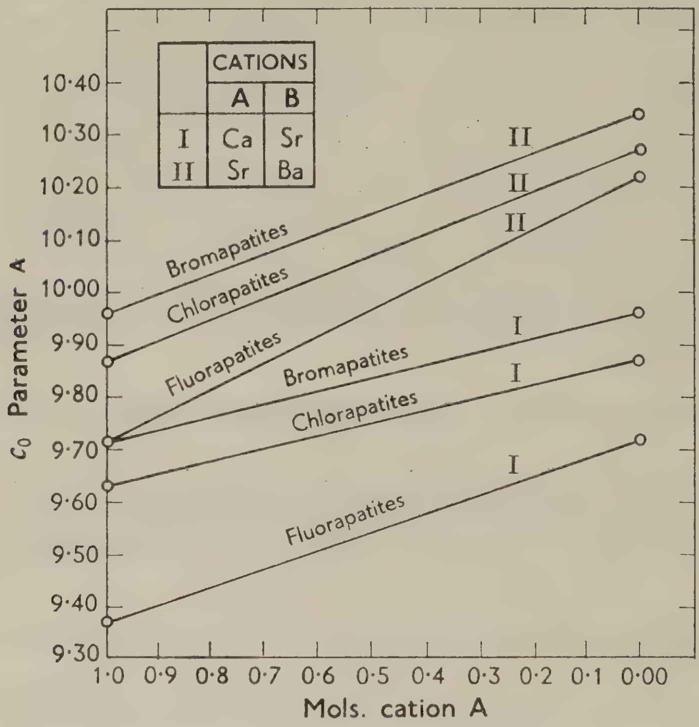


FIG. 11.—Variation of $a_0$-parameters with composition of alkaline-earth apatites

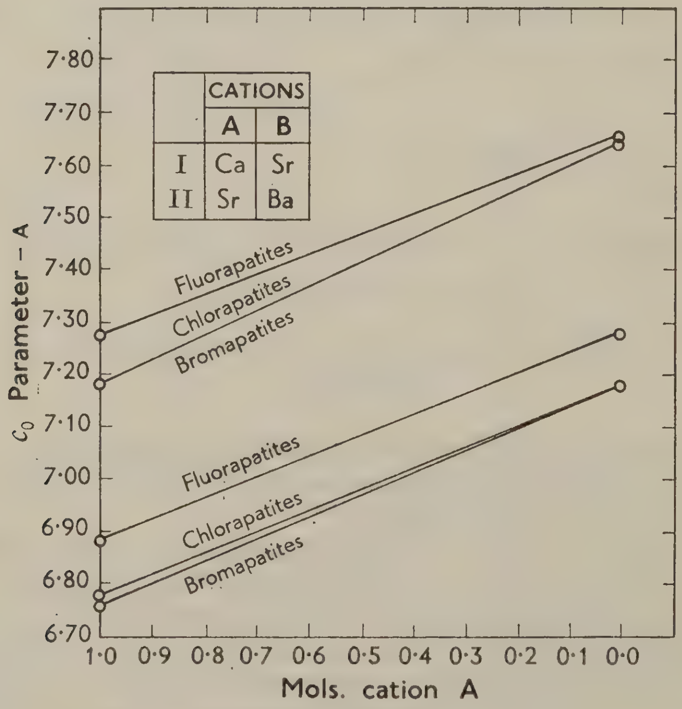


FIG. 12.—Variation of $c_0$-parameters with composition of alkaline-earth apatites

precipitation reactions using calcium and strontium nitrates and precipitating with diammonium phosphate solution in the presence of ethylenediamine. An excess of calcium and strontium ions (3 atoms per mole of phosphate) is necessary to give the required product.[250] The material is then dried and heated at 900°C. Drying of the

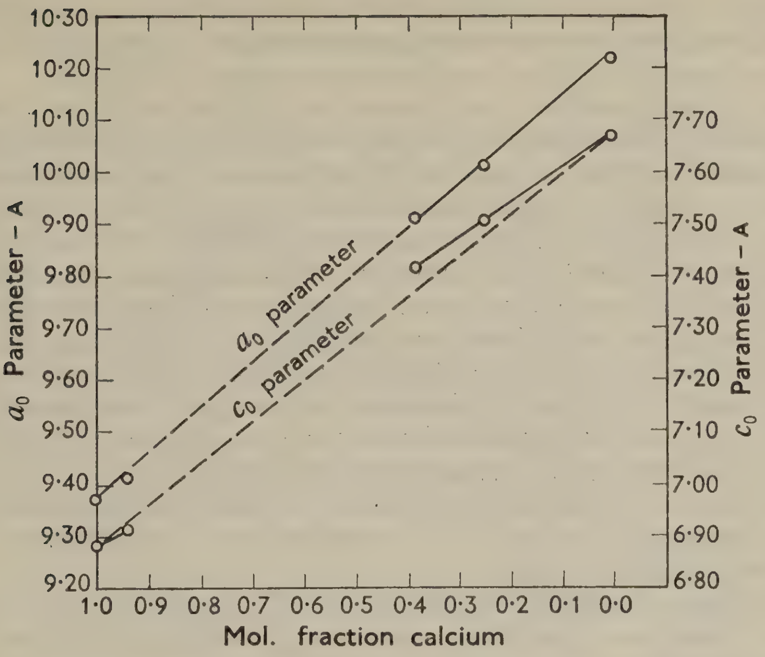


FIG. 13.—Variation of lattice constants in calcium–barium fluorapatites

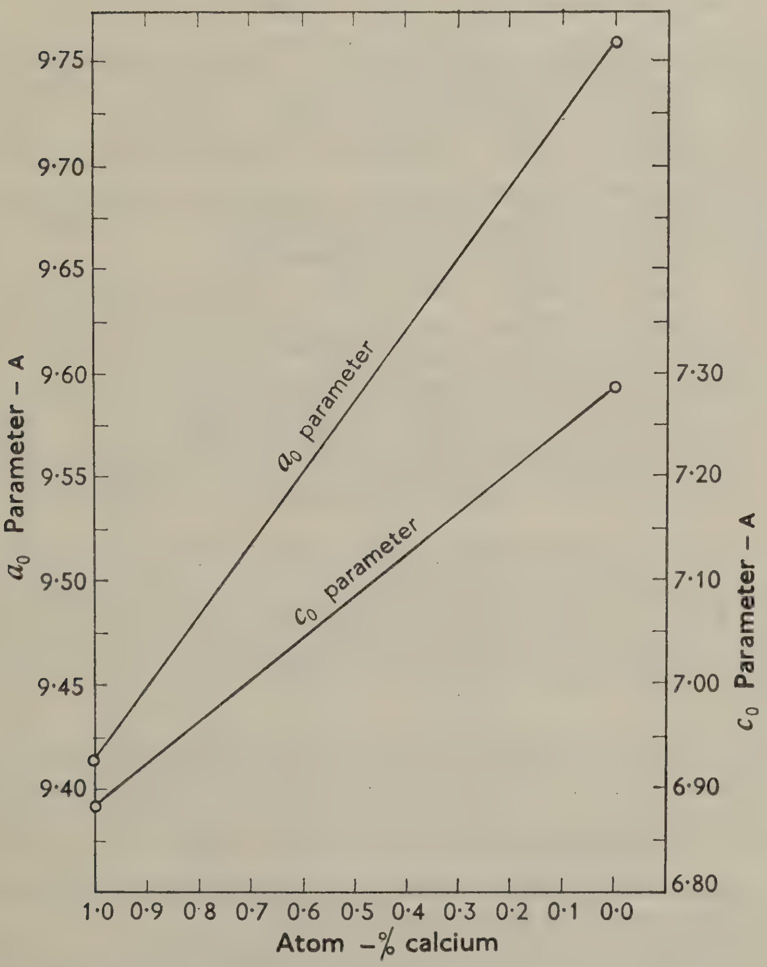


FIG. 14.—Lattice constants of mixed calcium–strontium hydroxyapatites

apatite at 110°C. without heating to 900°C. was satisfactory only if the calcium/strontium ratio was kept constant during precipitation.[251] The lattice constants were related to the composition in a linear manner as shown in Fig. 14.

Magnesium hydroxyapatite is not formed by the type of reaction used to obtain the alkaline-earth compounds. A product having a composition corresponding to $Mg_3(PO_4)_2,Mg(OH)_2,9H_2O$ is obtained by hydrolyzing magnesium monohydrogen phosphate for 6 weeks in 0·01N. sodium hydroxide at 37°C. Analysis and *X*-ray examination show that this is a basic magnesium phosphate and that it does not have an apatite structure.[252] On boiling a mixture of trimagnesium phosphate with excess of 0·01N. sodium hydroxide a hydrated product is obtained the analysis of which corresponds to a magnesium hydroxyapatite of formula $3Mg_3(PO_4)_2,Mg(OH)_2,xH_2O$. The degree of hydration is 11, 15 or $23H_2O$, according to the conditions of preparation. When heated to 500–600°C. the material becomes incandescent and forms a compound with an analysis agreeing with that of an oxyapatite, $3Mg_3(PO_4)_2,MgO$.[253] In a somewhat similar way a lithium hydroxyapatite, $3Li_3PO_4,LiOH$, is said to be formed by adding 1 mole of phosphoric acid to 6 or more moles of lithium hydroxide solution and boiling for 100 hr.[254] No *X*-ray evidence supporting the structure of these two compounds was given.

A cadmium hydroxyapatite, $3Cd_3(PO_4)_2,Cd(OH)_2$, has been made by reacting 2 g. of tricadmium phosphate, $Cd_3(PO_4)_2$, with 0·10 g. of cadmium hydroxide and 10 ml. of 0·10N. sodium hydroxide.[242]

Lead hydroxyapatite, $3Pb_3(PO_4)_2,Pb(OH)_2$, is obtained by hydrolyzing lead monohydrogen phosphate in 0·01N. sodium hydroxide for 7 days at 40°C. An alternative procedure is to heat a mixture of trilead phosphate and lead oxide at 950°C. in a stream of air saturated with water vapour, the reaction being[255]:

$$3Pb_3(PO_4)_2 + PbO + H_2O = 3Pb_3(PO_4)_2,Pb(OH)_2$$

A synthetic lead oxyapatite, $3Pb_3(PO_4)_2,PbO$, has been prepared from the components. *X*-Ray examination confirmed the apatite structure, the lattice constants being $a_0 = 9{\cdot}84$ A. and $c_0 = 7{\cdot}43$ A.[256] Subsequent phase studies of the $PbO–P_2O_5$ system and *X*-ray diffraction data indicated that half the halogen sites in the pyromorphite $[3Pb_3(PO_4)_2,PbCl_2]$ structure were occupied by oxygen ions. Since there was an ordered distribution of the latter in the lattice, the $c_0$ parameter was doubled, giving $a_0 = 9{\cdot}84$ A. and $c_0 = 14{\cdot}86$ A. as the constants.[257]

Replacement of the $PO_4$ groups in lead apatite by $SiO_4$ and $SO_4$ groups was shown to occur if an intermediate ion such as $Na^+$ was also present. This can give rise to apatite structures such as $Pb_4NaPO_4.SiO_4.SO_4$.[258] The pyromorphite type of apatite structure is still retained when all the phosphate groups have been replaced by silicate. The anions of these compounds are then composed solely of $SiO_4$ tetrahedra from which it appears that the halogen positions in the apatite structure are unoccupied or only partly occupied. These conditions have not been observed in the calcium apatites.[259]

Compounds of the type $3Pb_3(ZO_4)_2,PbX_2$, where Z = P, As or V and X = F, Cl, Br or I, have been prepared by sintering at 600°C. the stoicheiometric amounts of $Pb_3(ZO_4)_2$ and $PbX_2$. All these have an apatite structure and are stable in water except $3Pb_3(PO_4)_2,PbI_2$. The last compound appears to have an apatite structure in that it gives an *X*-ray pattern which does not show lines due to lead iodide or $Pb_3(PO_4)_2$.[260]

Alkali metal–lead apatites have been obtained by causing lead pyrophosphate to react with sodium carbonate in the presence of moisture. The compound $NaPb_4(PO_4)_3$ is formed, together with lead hydroxyapatite, $3Pb_3(PO_4)_2,Pb(OH)_2$. Under anhydrous conditions a sodium lead orthophosphate, $NaPbPO_4$, which does not have an apatite structure, is produced. The corresponding potassium compounds have been prepared by using potassium instead of sodium carbonate.[261]

A number of compounds having an apatite structure are known, in which the major cation is lead and the anion may be phosphate, arsenate, silicate, vanadate or sulphate. These were obtained from melts in which they were present as congruently melting compounds.[262] The lattice constants of these materials are given in Table XV.

*Table XV.—Lattice Constants of Some Lead Compounds having an Apatite Structure*

| Compound | Lattice constants, A. | |
|---|---|---|
| | $a_0$ | $c_0$ |
| $Pb_5GeO_4(PO_4)_2$ | 9·88 | 7·32 |
| $Pb_5(Si_{0\cdot5}Ge_{0\cdot5}O_4)(PO_4)_2$ | 9·81 | 7·30 |
| $Pb_5(Si_{0\cdot5}Ge_{0\cdot5}O_4)(PO_4)(AsO_4)$ | 9·92 | 7·34 |
| $Pb_5SiO_4.VO_4.PO_4$ | 9·88 | 7·33 |
| $Pb_5SiO_4(VO_4)_2$ | 9·99 | 7·35 |
| $Pb_5SiO_4(AsO_4)_2$ | 10·02 | 7·38 |
| $Pb_5GeO_4(VO_4)_2$ | 10·06 | 7·37 |
| $Pb_5GeO_4(AsO_4)_2$ | 10·10 | 7·40 |
| $Pb_4Na(PO_4)_3$ | 9·71 | 7·18 |
| $Pb_4K(PO_4)_3$ | 9·81 | 7·28 |
| $Pb_4Tl(PO_4)_3$ | 9·82 | 7·37 |
| $Pb_4Rh(PO_4)_3$ | 9·86 | 7·37 |
| $Pb_4Bi(SiO_4)_2(PO_4)$ | 9·76 | 7·26 |
| $Pb_3BiTl(SiO_4)(PO_4)_2$ | 9·78 | 7·34 |
| $Pb_{4\cdot5}Na_{0\cdot5}(PO_4)_{2\cdot5}(SiO_4)_{0\cdot5}$ | 9·76 | 7·25 |

### Naturally Occurring Phosphates

Phosphate minerals form a group with the arsenates and vanadates in which the structural units are trivalent tetrahedral $XO_4^{3-}$ groups. In these, partial or complete replacement of phosphorus by arsenic or vanadium is possible. Sulphate, chromate and silicate groups are also known to be present in some phosphorus minerals. There is, however, no series of minerals which directly links the phosphates with sulphate, chromate, silicate, tungstate and molybdate minerals in which divalent $XO_4^{2-}$ groups are present.

The known minerals, reported up to the end of 1965, which contain more than 1% of phosphorus, are given in Table XVI. Complete data, together with some physical and chemical properties, are given in Dana's *System of Mineralogy*[263] which describes minerals known up to 1951.

In Table XVI the minerals are given in order of the groups in the Periodic Table and according to the cation which is present in the greatest percentage. Exceptions have been made where isomorphous replacement of one element by another takes place. Formulæ are given for purposes of identifying a mineral and as an indication of the chemical composition of pure specimens. These formulæ do not necessarily refer to unit cell contents or other structural units.

The percentage composition refers to the analysis of authentic specimens of each mineral. Where several specimens, usually from different sources, have been analyzed, the variation in the analytical results is shown. Constituents which do not enter into the chemical composition but are present as impurities in the mineral, are not included in the analysis. Literature references are given only for those minerals which have been reported since 1951 and which are not described by Dana.

Several of the older known minerals have been re-examined more recently. This has been done where the previously accepted analysis or composition was open to doubt. These investigations are indicated below.

*Abukumalite* has been identified as a yttrium silico-phosphate.[264]

*Avelinoite and cyrilovite* have been shown to be identical,[265-6] the name cyrilovite having priority.[267] The mineral differs from *wardite* in containing iron instead of aluminium. The original analysis appears to be in error in that no sodium was reported.[268]

*Baldaufite, wenzelite and hureaulite* are listed as separate minerals in Table XVI. It has, however, been reported that these are identical, the name hureaulite having priority.[269]

*Britholite* is an older mineral[270] which has been characterized by more recent examination[271] and analysis.[272] A specimen found in Siberian pegmatites has been shown to be a rare earth silicophosphate having the following composition: $SiO_2$ 19·0, $P_2O_5$ 4·5, CaO 14·8, $ThO_2$ 9·8, $UO_3$ 2·1, $Ce_2O_3+La_2O_3+Y_2O_3$ 40·9, F 1·9 and $H_2O$ 3·0%. Associated with this mineral is a new variety, an alumino-britholite which analyzes as follows: $SiO_2$ 19–22, $P_2O_5$ 1·9–4·0, CaO 17·3–22·6, $ThO_2$ 4·8–9·3, $UO_3$ 0·6–2·1, $Ce_2O_3+La_2O_3+Y_2O_3$ 27·6–32·3, $Al_2O_3$ 9·5–14·9, $ZrO_2$ 1·0, $Fe_2O_3$ 0·4–5·4, F 1·4–1·7 and $H_2O$ 0·6–1·5%. It has an apatite structure in which the parameters of the unit cell are $a_0=9{\cdot}47$ A. and $c_0=6{\cdot}95$ A.

Comparison of britholite with *beckelite* ($SiO_2$ 17·1–20·4, $P_2O_5$ 3·25, CaO 11·4–15·5, $Ce_2O_3$ 28·1, $La_2O_3$ 27·8–31·6, $Y_2O_3$ 2·9–3·5, $ZrO_2$ 2·5, $ThO_2$ 0·9 and $H_2O$ 2·6%) and *lessingite* ($SiO_2$ 19·9, $P_2O_5$ 1·1, CaO 11·7, $Ce_2O_3$ 22·5, $La_2O_3$ 36·7, $Y_2O_3$ 3·4, $Al_2O_3$ 0·3, $Fe_2O_3$ 0·65, MnO 0·9, $CO_2$ 0·4, F 0·5 and $H_2O$ 1·9%) and *X*-ray examination of the three minerals show that they belong to the same mineral species.[273] A more recent examination[393] of a specimen containing more $P_2O_5$ than $SiO_2$ gave the analysis $P_2O_5$ 17·0, $SiO_2$ 12·3, CaO 28·8, $ThO_2$ 5·6, F 2·1, and rare earth oxides 33·4%. This corresponds to the formula $(Ca,Ce,Th)_5(PO_4,SiO_4)_3,OH,F$.

*Churchite and weinschenkite.* Churchite was originally thought to contain cerium, but a later analysis[274] showed that the rare earth element present in the mineral was yttrium. It was also shown[275] that it was identical with another phosphate known as *weinschenkite*. The name *churchite* has priority.

*Dewindite* appears to be a doubtful mineral.[276] It was originally formulated as a lead compound, $Pb_3(UO_2)_5(PO_4)_4(OH)_4,10H_2O$,[277] but was later shown to have an analysis corresponding closely to $Pb_3(UO_2)_6(PO_4)_4(OH)_6,9H_2O$.[278] Although it is known to be iso-structural with *phosphuranylite* and *renardite*, the chemical formulæ are not analogous.[279]

*Florencite.* A more recent analysis has given: $P_2O_5$ 26·0, $Al_2O_3$ 29·8, $Ln_2O_3$ 17·6, SrO 9·0, CaO 1·6, $SO_3$ 1·7, F 1·6 and $H_2O$ 12·9% from which the specimen was formulated as $(Ce,Sr,Ca)(PO_4,SO_4)_2.Al_3(F,OH)_6,H_2O$.[387, 388] The mineral belongs to the *goyazite* series which includes *crandallite*, *gorceixite*, *goyazite* and *florencite*.[6, 388]

*Hopeite.* The crystal structure of this mineral, $Zn_3(PO_4)_2,4H_2O$, has been shown to have a close relation to that of *phosphophyllite*, $Zn_2Fe(PO_4)_2,4H_2O$.[428]

*Huttonite.* Compounds of the type $M^{II}Th(PO_4)_2$ have a huttonite ($ThSiO_4$) structure.[429]

*Leucophosphite.* Early analyses showed that significant amounts of aluminium were present in this mineral, but a re-examination of a purer specimen showed only minor amounts of this metal.[280] The formula and composition have been reported as being those shown in Table XVI. It has also been reported that the mineral contains ammonium ion,[281] but again the analysis was of an impure specimen. A synthetic material has been made.[282] On the other hand more recent *X*-ray studies[297] have suggested that the formula is $(K,NH_4)(Al,Fe)_2(OH)(PO_4)_2,2H_2O$.

*Liroconite* is strictly an arsenate mineral, but some specimens contain a small percentage of phosphorus.

*Lomonosovite.* New data indicate that this mineral may be nearer in composition to the formula $Na_2MnTiSi_4O_{16},2Na_3PO_4$ than the earlier one given in Table XVI. It is also claimed that a meta-lomonosovite, $Na_3H_3MnTiSi_4O_{18},2NaPO_3$, exists.[283–4]

*Messelite* is similar to *collinsite* with an analysis corresponding to $(Ca,Fe,Mn,Mg)_3(PO_4)_2,3H_2O$.[285] The mineral has also been considered to be *anapaite* partly altered to *collinsite*.[394] The formula $Ca_2Fe(PO_4)_2,3H_2O$ has been reported.[395]

*Mitridatite* appears to have a variable composition in which calcium and iron are present in varying proportions, and phosphate is partly replaced by hydroxyl. It has been suggested[286] that the general formula is $Ca_2Fe_3(PO_4)_{3-x}(OH)_{4+3x},nH_2O$.

*Morinite* was originally given the formula $Na_2Ca_3Al_3H(PO_4)_4,F_6,8H_2O$. Subsequent variations were $(Ca,Na)_3Al_2(PO_4)_2.(F,OH)_6,H_2O$,[287] $(Na,Ca,Al)_2(PO_4)_2F_3(OH)_2, 1\frac{1}{2}H_2O$[288] and $Na_2Ca_4Al_4(PO_4)_4(F,OH)_{10},3H_2O$.[289] A more recent examination of a purer specimen including chemical and thermal analysis studies gives the composition as $Na_2(Ca,Al)_4(F_6,O_2)(PO_4)_4,5H_2O$.[290]

*Phosphophyllite.* The structure of this mineral, having the composition $Zn_2Fe(PO_4)_2, 4H_2O$, has been determined.[420]

*Phosphuranylite* is an older known mineral which was initially given the empirical formula $3UO_2,P_2O_5,6H_2O$. Later analysis[277] showed that it contained calcium and had a composition which was close to $Ca(UO_2)_7(OH)_4(PO_4)_4,10H_2O$. Subsequently it was shown to be $Ca(UO_2)_4(OH)_4(PO_4)_4,7H_2O$.[278–9] This has now been confirmed by more detailed examination and synthesis of the mineral.[276]

*Roscherite.* From the original analysis the mineral was thought to contain aluminium and was given the composition $(Ca,Mn,Fe)_2AlOH(PO_4)_2,2H_2O$. Newer data and a re-examination of the analytical procedure used in the original analysis showed that the trivalent metal present was beryllium and not aluminium. The correct formula was found to be $(Ca,Mn,Fe)_3(BePO_4)_3(OH)_3,2H_2O$.[291]

*Saléeite.* A more recent examination of specimens of this mineral, giving further analytical data to those of Table XVI, confirms the previous findings.[292–3]

*Scorzalite, lazulite and barbosalite.* These three minerals have recently been shown to be iso-structural.[294] The common structure consists of octahedra of oxygen and metal ions which are packed with $PO_4$ tetrahedra to give a unit cell content of $(Fe,Mg)_2(Al,Fe)_4(PO_4)_4(OH)_4$. The individual structures are as follow:

| | |
|---|---|
| *Scorzalite* | $Fe_{1\cdot 53}Mg_{0\cdot 47}Al_4(PO_4)_4(OH)_4$ |
| *Lazulite* | $Fe_{0\cdot 23}Mg_{1\cdot 77}Al_4(PO_4)_4(OH)_4$ |
| *Barbosalite* | $Fe_2Fe_4(PO_4)_4(OH)_4$ |

*Taranakite.* Analytical and other data have been reported more recently for this mineral, and show the presence of up to 2% $Fe_2O_3$. It is identical with the minerals *minervite* and *palmerite* which were discovered later, but is distinct from *minyulite* and other potassium aluminium phosphates.[295–6] *X*-Ray studies[297] and synthetic preparations[136, 137] show that the formula is $H_6(K,NH_4)_3Al_5(PO_4)_8,18H_2O$. The one given previously, $K_2Al_6(OH)_2(PO_4)_6,18H_2O$, was originally considered to be doubtful (reference 263, p. 999).

*Vauquelinite.* Analysis of a Russian specimen[363] gave the following results: $P_2O_5$ 0–8·7, CuO 10·3–11·9, PbO 61·1–67·6, $Cr_2O_3$ 26·8–17·4, $Fe_2O_3$ 0–0·7% corresponding to a mixture of copper and lead chromates and phosphates represented by $n[3(Pb,Cu)O(P_2O_5)_2]+m[(Pb,Cu)O(CrO_3)_2]$. A subsequent examination[364] suggested that the mineral was a solid solution of chromates and phosphates and formulated as $(Cu,Pb)_3[CrO_4,PO_4]_2$. The mineral is also known under the name *laxmannite*.

*Viséite* was originally[299] given the formula $3SiO_2,3P_2O_5,5Al_2O_3.5CaO,nH_2O$ with $n=25$–30. A more recent examination[300] shows that the structure and optical and physical properties are closely related to analcime. The mineral is a zeolite, formulated as $Na_2Ca_{10}(Al_{20}Si_6P_{10}H_{36})O_{46},16H_2O$.

*Wardite* was originally supposed to contain calcium and to have the formula $Na_4CaAl_{12}(PO_4)_8(OH)_{18},6H_2O$. Later examination,[265] however, showed that the calcium was an impurity and was not present in the unit cell.[298]

Many of the phosphorus minerals described in the earlier literature are of doubtful validity or have since been discredited for various reasons. The following list gives details and notes on these minerals. The page numbers in this list refer to Dana's *System of Mineralogy*.[263]

*Amphithalite* is an aluminium calcium phosphate containing $Al_2O_3$ 48·5, CaO 5·8, MgO 1·6, $P_2O_5$ 30·1 and $H_2O$ 12·5%. The validity and analysis, however, require verification (p. 873).

*Asovskite*. The analysis $P_2O_5$ 15·9–17·0, $Fe_2O_3$ 52·7–57·2, MnO 0–1·7, and $H_2O$ 23·2–25·8% corresponds to a basic ferric phosphate $Fe_3PO_4(OH)_6$,[396] but the mineral needs verification (p. 795).

*Attacolite*. The analysis of a specimen of doubtful authenticity was $Al_2O_3$ 29·8, MnO 8·0, $Fe_2O_3$ 4·0, CaO 13·2, $Na_2O$ 0·5, $P_2O_5$ 36·1 and $H_2O$ 6·9%. This corresponds roughly to the formula $(CaMn)_3Al_4(PO_4)_4(OH)_6$ (p. 845). A more recent examination confirms the validity of the mineral, and analysis gave $P_2O_5$ 32·6, $SiO_2$ 9·4, $Al_2O_3$ 27, FeO 1·3, MnO 7·1, CaO 11·4, SrO 3·3, and $H_2O$ 5·9%.[397] The suggested formula is $(Ca,Sr,Mn)_3(Al,Fe,Mn)_6(PO_4,SiO_4)_{7-m}(OH)_{4m},3H_2O$.

*Barrandite* is an aluminian form of *strengite* (p. 756).

*Bialite*. This is a magnesian variety of *tavistockite*.[398] The latter name has priority (p. 906).

*Bolivarite*. The analysis, $Al_2O_3$ 44·1, $P_2O_5$ 34·9 and $H_2O$ 20·6%, agrees with $Al_2PO_4(OH)_3,H_2O$ approximately, but verification is required (p. 872).[302, 301]

*Borickite*. The analysis, $Fe_2O_3$ 52·3–53·0, CaO 7·3–8·2, $P_2O_5$ 19·4–20·5, $H_2O$ 19·1–20·0%, gives a formula approximating to $CaFe_5(PO_4)_2(OH)_{11},3H_2O$. The mineral, however, is ill-defined and is similar in many respects to *delvauxite* (p. 915).[367]

*Bosphorite* is a variety of *vivianite* (p. 744).

*Calcioferrite*. The analytical data are $Fe_2O_3$ 24·3, CaO 14·7, MgO 2·7, $Al_2O_3$ 2·9, $P_2O_5$ 34·0 and $H_2O$ 20·6%. Neglecting the small percentages of magnesium and aluminium, the data give the uncertain formula $Ca_3Fe_3(PO_4)_4(OH)_3,8H_2O$ (p. 976).

*Callainite* is very similar to *variscite* and has the analysis $Al_2O_3$ 29·6, $Fe_2O_3$ 1·8, CaO 0·7, $P_2O_5$ 42·6 and $H_2O$ 23·6% (p. 761).

*Cirrolite* approximates to $Ca_3Al_2(PO_4)_3(OH)_3$ from the analysis CaO 29·5, $Al_2O_3$ 20·5, MnO 2·2, FeO 0·9, $P_2O_5$ 41·2 and $H_2O$ 5·1%. On the other hand evidence as to the validity of the mineral as a species is lacking (p. 845).

*Coeruleolactite* is a hydrated basic aluminium phosphate of uncertain formula, probably $Al_3(PO_4)_2(OH)_3,4H_2O$, which, however, omits the copper found in the analysis: $Al_2O_3$ 35·1–38·7, CuO 1·4–4·3, CaO 0–2·4, $P_2O_5$ 36·3 and $H_2O$ 21·5% (p. 961).

*Dittmarite* has an analysis of MgO 25·7, $(NH_4)_2O$ 3·9, $P_2O_5$ 46·5 and $H_2O$ 23·4%, which is close to the formula $Mg_5(NH_4)H_4(PO_4)_5,8H_2O$. It is found in bat guano together with *struvite*, *newberyite* and *hannayite* (p. 699).

*Eguéite* is a hydrated ferric phosphate in which some iron is replaced by calcium and aluminium. The analysis, $Fe_2O_3$ 44·2, CaO 2·3, $Al_2O_3$ 1·5, $P_2O_5$ 30·3 and $H_2O$ 20·5%, gives the formula $(Ca,Al)Fe_{14}(PO_4)_{10}(OH)_4,21H_2O$ (p. 955).

*Ferrazite* is a hydrated lead, barium, aluminium phosphate. The analysis, which needs checking, gave PbO 45·6, BaO 8·9, $Al_2O_3$ 3·5, $SiO_2$ 2·4, $P_2O_5$ 26·2 and $H_2O$ 14·2% (p. 832).

*Fischerite*. An analysis gave $Al_2O_3$ 38·5, $Fe_2O_3$ 1·2, CuO 0·8, $P_2O_5$ 29·0 and $H_2O$ 27·5%. The mineral is, however, very similar to *wavellite* (p. 762). Both give the same *X*-ray powder diagram[303–4] but the optical and physical properties of the two minerals are different.[304] Wavellite has been formulated as $4AlPO_4,2Al(OH)_3,9H_2O$ and fischerite as $2AlPO_4,2Al(OH)_3,5H_2O$[304] or $2AlPO_4,Al(OH)_3,5H_2O$[303] (p. 762).

*Foucherite* contains $Fe_2O_3$ 38·5, CaO 7·7, $Al_2O_3$ 4·5, $P_2O_5$ 19·5 and $H_2O$ 28·5%, which corresponds to the formula $Ca(Fe,Al)_4(PO_4)_2(OH)_8,7H_2O$. Its characteristics are similar to those of *borickite* (p. 915).[367]

*Globosite* is very similar to *strengite*. Analysis gave $Fe_2O_3$ 40·9, MgO 2·4, CaO 2·4, $P_2O_5$ 28·9 and $H_2O$ 23·9% (p. 762).

*Harbortite* has the analysis $Al_2O_3$ 33·4, $Fe_2O_3$ 3·8, $Na_2O$ 3·7, CaO 1·2, $SnO_2$ 2·8, $TiO_2$ 1·0, $P_2O_5$ 35·7 and $H_2O$ 18·3%, approximating to $Al_3(PO_4)_2(OH)_3,3H_2O$. The validity of the mineral is doubtful and its *X*-ray pattern resembles that of turquoise (p. 951).

*Hibbenite*, with a composition corresponding to $Zn_7(PO_4)_4(OH)_2,7H_2O$, resembles *hopeite* and *spencerite* and may be a mixture of these (p. 737).

*Jezekite*. More recent *X*-ray examination[272, 361] suggests that this mineral is identical with *morinite*. The latter name has priority (p. 784).

*Kehoeite* needs verification (p. 944).

*Kolbeckite* is a hydrated aluminium, beryllium and calcium silicophosphate of uncertain formula. The analysis is $Al_2O_3$ 21·4, BeO 8·7, CaO 3·2, $SiO_2$ 9·3, $P_2O_5$ 33·8 and $H_2O$ 23·5% (p. 1015).

*Koninckite*, $FePO_4,3H_2O$, with an analysis of $Fe_2O_3$ 34·4, $Al_2O_3$ 4·6, $P_2O_5$ 34·8 and $H_2O$ 26·2% needs further study (p. 763). It appears to be derived from *heterosite* by simple hydration[373] (p. 763).

*Kribergite*. The approximate formula for this is $Al_{16}(PO_4)_8(SO_4)_3(OH)_{18},10H_2O$, corresponding to the analysis $Al_2O_3$ 38·5, $SO_3$ 13·1, $P_2O_5$ 31·3 and $H_2O$ 17·2% (p. 1011).

*Lacroixite*. The formula of this mineral is unknown. The analysis is CaO 19·5, $Al_2O_3$ 18·9, $Na_2O$ 14·9, MnO 8·4, $SiO_2$ 0·9, F 6·5, $P_2O_5$ 28·8 and $H_2O$ 5·46% (p. 783).

*Merrillite* has an analysis corresponding to $Na_2Ca_3O(PO_4)_2$[399] and may be a variety of *francolite*[400] (p. 797).

*Meyersite*, the analysis of which is given as 66·3% $AlPO_4$, 2·5% $FePO_4$ and 26·1% $H_2O$, is probably *ferrian variscite* (p. 761).

*Planerite* contains $Al_2O_3$ 37·5, CuO 3·7, FeO 3·5, $P_2O_5$ 33·9 and $H_2O$ 20·9%. It could be identical with *fischerite* or *coeruleolactite* (p. 762).

*Millisite* $(Na,K,Ca)Al_6(PO_4)_4(OH)_9,3H_2O$ is iso-structural with and is related to *wardite* (p. 941).

*Redondite*. The older analysis, $P_2O_5$ 43·2, $Al_2O_3$ 16·6, $Fe_2O_3$ 14·4, CaO 0·6 and $H_2O$ 24·0% indicated that the mineral was a ferrian variety of *variscite* (p. 756). A later analysis gave $P_2O_5$ 42·5, $Al_2O_3$ 29·25, $Fe_2O_3$ 3·5, $Cr_2O_3$ 1·11 and $H_2O$ 22·7%, corresponding to the formula $(Al,Fe,Cr)PO_4,2H_2O$.[401] A more recent analysis $P_2O_5$ 40·7, $Al_2O_3$ 34·65, $Fe_2O_3$ 0·34 and $H_2O$ 16·8%, and *X*-ray examination suggest that the mineral is distinct from *variscite*.[402] However, this view has been criticized[403] (pp. 756, 759).

*Richellite* has an uncertain formula, probably $Ca_3Fe_{10}(PO_4)_8(OH)_{12},nH_2O$ and an analysis of $Fe_2O_3$ 28·7–29·7, $Al_2O_3$ 1·8–3·6, CaO 5·5–7·2, F 1·0–6·0, $P_2O_5$ 25·5–28·8 and $H_2O$ 29·4–33·0 (p. 956).

*Richmondite* appears to be $AlPO_4,4H_2O$, with an analysis of $Al_2O_3$ 26·7, $P_2O_5$ 37·6 and $H_2O$ 35·7% (p. 762), but has been discredited as a separate species. The name is also used for a sulphide mineral[371] (p. 762).

*Rosieresite* is a hydrated copper aluminium lead phosphate, a specimen of which gave the analysis: $Al_2O_3$ 23·0, PbO 10·0, CuO 3·0, $P_2O_5$ 25·5 and $H_2O$ 38·0% (p. 924).

*Salmonsite* contains MnO 37·7, $Fe_2O_3$ 9·5, $P_2O_5$ 34·9 and $H_2O$ 15·7%, which could be formulated as $Mn_9Fe_7(PO_4)_8,14H_2O$. The mineral may, however, be an alteration product of *hureaulite* and its validity needs verification (p. 730).

*Sarcopside*. The formula of this is uncertain but may be $(Fe,Mn,Ca)_7(PO_4)_4F_2$ corresponding to the analysis of MnO 10·8–20·6, FeO 30·5–44·5, $Fe_2O_3$ 1·7–8·8, CaO 3·4–4·7, F 4·4–4·7, $P_2O_5$ 33·3–35·7 and $H_2O$ 1·5%. It might be an alteration product of *vivianite* (p. 858).[370] Another examination[404] indicated the formula $(Fe,Mn,Ca)_3(PO_4)_2$, but no calcium was found in a later analysis, the results being $P_2O_5$ 39·7, FeO 50–51·0, MnO 6·2–6·9 and MgO 2·7–3·5%. These results correspond to the formula $(Fe,Mn,Mg)_3(PO_4)_2$. The earlier confusion is attributed to contamination of the specimens with CaO derived from intergrowth with the similar mineral *graftonite*[405] (p. 858).

*Schertelite* is found in bat guano together with *struvite* and *newberyite*. The analysis, MgO 12·2, $(NH_4)_2O$ 16·2, $P_2O_5$ 43·9 and $H_2O$ 27·6% corresponds closely to $Mg(NH_4)_2H_2(PO_4)_2,4H_2O$ (p. 699). A synthetic product having this formula has been made[369] (p. 699).

*Spodiosite* may be analogous to *wagnerite*. The mineral is ill-defined, and the analysis, which is uncertain, is given as CaO 45·8–49·8, MgO 2·3–8·6, $Fe_2O_3$ 1·2–2·4, $SiO_2$ 1·2–8·7, $CO_2$ 0–3·9, F 2·9–4·7, $P_2O_5$ 29·6–32·2 and $H_2O$ 2·7–3·8% (p. 848).

*Stewartite* is a hydrated manganese phosphate of uncertain composition and is probably an alteration product of *lithiophilite* (p. 730). More recent examination indicates the probable formula $MnFe_2OHPO_4,8H_2O$.[374] Chemical analyses,[375–6, 368] physical and optical properties,[375, 368, 301] differential thermal analyses[368] and *X*-ray data have been reported.[301, 376] *Stewartite* is an alteration product of *triphylite* and has a unit cell very close to that of *laueite*[379] (p. 730).

*Tinticite*. The analysis is: $Fe_2O_3$ 48·8–49·2, $SO_3$ 0·7–1·1, $P_2O_5$ 28·4–30·2 and $H_2O$ 18·9–19·7% corresponding to $Fe_3(PO_4)_2(OH)_3,3\frac{1}{2}H_2O$ (p. 970). Infra-red analysis shows that it is distinct from *beraunite*[386] (p. 970).

*Trolleite* has the analysis $P_2O_5$ 46·7, $Al_2O_3$ 43·3, $Fe_2O_3$ 2·75, CaO 1·0 and $H_2O$ 6·2%, which is close to the formula $Al_4(PO_4)_3(OH)_3$. Validity of the species is lacking (p. 911).

*Vashegyite* has an analysis of $Al_2O_3$ 26·5–28·3, $Fe_2O_3$ 1·2–1·3, $P_2O_5$ 26·6–31·3 and $H_2O$ 39–44·7%, giving the somewhat uncertain formula $Al_4(PO_4)_3(OH)_3,nH_2O$ (p. 999).[373]

*Zepharovichite* is probably identical with *wavellite*, the analysis being: $Al_2O_3$ 28·4–29·8, CaO 0·5–1·4, $SiO_2$ 0·5–6·1, $P_2O_5$ 35·6–37·8 and $H_2O$ 26·6–29·0% (p. 964).[372]

Some of the more recently reported minerals have not been definitely established. The more important of these are commented on below.

*Chavesite* is a hydrated calcium manganese phosphate which is isostructural with and very similar to *monetite*.[417]

*Palermoite*. Examination of a purified specimen gave the analysis $P_2O_5$ 42·9–46·4, $Al_2O_3$ 30·8–33·9, SrO 9·2–12·9, CaO 0·9–1·4, $Na_2O$ 1·3–1·6 and $Li_2O$ 3·7–4·0%, corresponding to the formula $(Li,Na)_2(Ca,Sr)(Al,OH,PO_4)_4$.[406] This is stated to be in better agreement with the unit cell contents and the structure of the mineral than previous suggestions.[307–8]

*Tangaite*. This name has been suggested for a mineral similar to *variscite*.[401–2] However, it is reported to be superfluous because tangaite is identical with *redondite*.[403] The analysis is given as $P_2O_5$ 42·5, $Al_2O_3$ 29·3, $Fe_2O_3$ 3·5, $Cr_2O_3$ 1·1, CuO 0·9 and $H_2O$ 22·7%.[401]

*Rhabdophane minerals*. The only well-established members of this group are *rhabdophane* $(Ce,La)PO_4,H_2O$ and *ningyoite* $(Ca,Ce,U)PO_4,H_2O$. Minerals to which the names *silico-rhabdophane*, *titano-rhabdophane* and *silico-smirnovskite* have been given, are reported to have the following analyses:

| | Silico-rhabdophane | Titano-rhabdophane | Silico-smirnovskite |
|---|---|---|---|
| $P_2O_5$ | 18·8% | 3·6–6·8% | 3·1% |
| $SiO_2$ | 13·9 | 8·8–25·0 | 21·4 |
| $TiO_2$ | 0·4 | 12·3–13·1 | 2·9 |
| $Ce_2O_3$, etc. | 35·8 | 16·7–48·5 | 3·6 |
| $ThO_2$ | 0·3 | 0·8–6·0 | 45·3 |
| CaO | 3·4 | 3·1–3·2 | 2·9 |
| $Al_2O_3$ | 8·1 | 1·4–5·2 | — |
| $Fe_2O_3$ | 4·0 | 0·5–1·1 | 1·9 |
| $H_2O$ | 12·1 | 15·1–19·5 | 15·7 |
| $Nb_2O_5$ | 0·2 | 2·2–2·9 | — |

The separate names appear to be unnecessary because the minerals fit in well with *rhabdophane*, *monazite* or *smirnovskite*.[377] The name *tundrite* has been suggested for *titano-rhabdophane*, $Ce_2Ti(SiO_4,PO_4)(OH)_6,4H_2O$.[407]

*Hydrocerite.* Further examination and data are required to support the identity of this material. The analysis is very close to that of *smirnovskite* or *karnasurtite*.[378]

*Grayite.* The *X*-ray data would fit a mineral in either the *rhabdophane* or *monazite* group.[377]

*Karnasurtite* may be related to *monazite* or *rhabdophane*.[377]

*Erikite* with an analysis of $P_2O_5$ 20·1, $SiO_2$ 10·8, $Ce_2O_3$ 21·1, $La_2O_3$ 29·2, CaO 1·9, $Fe_2O_3$ 1·8, $ThO_2$ 1·2 and $H_2O$ 7·4% has been given the formula (La,Ce,Ca,Th,Fe) $(PO_4,SiO_4),H_2O$.[380] It seems, however, that the mineral belongs to either the *monazite* or *rhabdophane* group and the name is unnecessary.[381, 380]

*Fenghuangite.* The composition $(Ca,Ce,La,Th)_5(SiO_4,CO_4,PO_4)_3,O,OH,2{\cdot}5H_2O$ has been reported[382] for this mineral. This corresponds to the analysis: $P_2O_5$ 6·3, $SiO_2$ 13·8, $CO_2$ 2·6, $ThO_2$ 19·6, $CeO_2$ 13·0, $\Sigma\, Ce_2O_3$ 20·1, CaO 10·4 and $H_2O$ 5·5%, but the material is believed to be *thorian britholite*.[383]

*Jiningite.* This appears to be an unnecessary name for *thorite* or a variety of *thorogummite*.[384] The analysis is reported[384] to be: $P_2O_5$ 6·1, $SiO_2$ 7·1, $V_2O_5$ 1·0, $U_3O_8$ 0·5, $ThO_2$ 44·8, $ZrO_2$ 1·0, CaO 7·4, $Fe_2O_3$ 17·3, $Al_2O_3$ 1·5, $H_2O$ 9·9 and rare earth oxides $R_2O_3$ 1·8%.

*Shen-t'u shih.* Although the composition agrees with the formula

$$(Th,Fe,Ca,Ce)(SiO_4,PO_4,AsO_4)CO_3,OH,H_2O$$

the mineral appears to be a variety of *thorite* or *thorogummite*.[385] The reported analysis is: $P_2O_5$ 5·2, $SiO_2$ 15·8, $As_2O_5$ 3·6, $CO_2$ 1·85, $ThO_2$ 52·8, $Fe_2O_3$ 8·2, CaO 2·7, $\Sigma\, Ce_2O_3$ 2·1, $(NbTa)_2O_5$ 1·2 and $H_2O$ 3·4%.[385]

*Strontium-apatite.* It is suggested[391] that it would be better to use the name *belovite* for strontium-containing apatites.

*Pravdite.* This is an aluminium calcium silicate which contains a small percentage of phosphorus. The analysis is: $P_2O_5$ 3·1, $SiO_2$ 18·8, $Al_2O_3$ 35·7, CaO 15·8, $ThO_2$ 4·9, $Fe_2O_3$ 1·8 and rare earths 18·4%, corresponding to $Ca_4R.E._2Al_{10}Si_5O_{32}$.[392]

*Fornacite.* $(Pb,Cu,Fe)_3(CrO_4,AsO_4,PO_4)_2,OH$ is chemically and structurally related to *vauquelinite* (p. 652).

*Pseudo-autunite.* The formula derived from the analysis is given as

$$Ca_{0{\cdot}86}(UO_2)_{1{\cdot}14}(PO_4)_2(H_3O)_2,2{\cdot}5H_2O$$ [418]

This is valid only if $NH_4$ is known to be absent. The name has been criticized on the basis that chemical and *X*-ray examinations do not agree with the mineral being a member of the autunite or meta-autunite series.[419]

The minerals described since 1951 are given at the end of Table XVI, pages 46–55.

Further information on the occurrence, geochemistry and optical and other properties of most of the minerals in Table XVI is given by Gmelin.[408]

Table XVII lists the minerals in alphabetical order, together with the approximate $P_2O_5$ content, and the pages on which they are described. Where an analysis was not available, the $P_2O_5$ content, indicated by an asterisk, has been calculated from the formula.

## Table XVI.—Phosphorus Minerals

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Li_2O$ | $Na_2O$ | $(NH_4)_2O$ | CaO | MgO | FeO | $Fe_2O_3$ | MnO | $Al_2O_3$ | F | $H_2O$ |
| Triphylite | $LiFePO_4$ | 41·1–46·4 | 7–8·9 | — | — | — | — | 21·7–35·1 | — | 3·1–21·1 | — | — | — |
| Lithiophylite | $LiMnPO_4$ | 43·4–45·1 | 5·5–9·2 | — | — | — | — | 3·0–12·6 | — | 30·5–42·6 | — | — | — |
| Sicklerite | $LiMnFe(PO_4)_2$ | 43·1–44·8 | 3·8–4·9 | — | — | — | — | — | 4·7–14·6 | 26·1–33·6 | — | — | — |
| Ferri-sicklerite | $LiFeMn(PO_4)_2$ | 44·7 | 3·3–3·7 | — | — | — | — | — | 27·2–29·1 | 15·2–19·1 | — | — | — |
| Amblygonite | $(LiNaAl)_4(PO_4.F.OH)_4,H_2O$ | 43·4–48·2 | 6·7–9·6 | 0·6–5·3 | — | — | — | — | — | — | 33·6–37·6 | 9–11·3 | 0–2·2 |
| Montebrasite | $(LiNaAl)_4(PO_4.F.OH)_4,H_2O$ | 46·7–47·8 | 8·8–9·7 | 0·4–2·2 | — | — | — | — | — | — | 33·9–35·8 | 0·6–5·5 | 3·3–6·0 |
| Natromontebrasite | $(LiNaAl)_4(PO_4.F.OH)_4,H_2O$ | 44·4 | 3·2 | 11·2 | — | — | — | — | — | — | 33·6 | 4·5 | 5·6 |
| Natrophylite | $NaMnPO_4$ | 41·0 | — | 17·9 | — | — | — | — | — | 41·1 | — | — | — |
| Huhnerkobelite | $(NaCa)(FeMn)_2(PO_4)_2$ | 39·4–41·9 | — | 3·7–9·7 | — | 1·4–9·7 | — | 7·1–18·2 | 14·5–26·5 | 6·4–9·8 | — | — | — |
| Varulite | $(NaCa)(FeMn)_2(PO_4)_2$ | 42·8–44·9 | — | 7·1–9·7 | — | 2·3–4·9 | — | 7·5–12·0 | 5·3–8·4 | 21·1–25·3 | — | — | — |
| Alluaudite | $NaMnFe(PO_4)_2$ | 41·3–42·5 | — | 5·5–8·2 | — | 0–2·7 | — | — | 20·6–25·6 | 20·7–23·1 | — | — | — |
| Mangan–alluaudite | $NaMnFe(PO_4)_2$ | 40·9–46·7 | — | 6·9–8·4 | — | 2·2–4·6 | — | — | 12·8–19·8 | 26·2–28·2 | — | — | — |
| Arrojadite | $Na_2(FeMn)_5(PO_4)_4$ | 34·3–40·0 | — | 4·7–6·4 | — | — | — | 19·8–28·2 | — | 12·3–15·8 | — | — | — |
| Dickinsonite | $Na_6H_2(MgCaFeMn)_{14}(PO_4)_{12},H_2O$ | 39·6–40·9 | — | 7·4 | — | 2·1 | 1·7 | 12·3–13·3 | — | 31·7 | — | — | 1·6–1·8 |
| Fillowite | $Na_6H_2(CaFeMn)_{14}(PO_4)_{12},H_2O$ | 39·1–39·7 | — | 5·4–5·7 | — | 3·6–4·1 | — | 9·3–9·7 | — | 39·4–39·6 | — | — | 1·6–1·7 |
| Lacroixite | $Na_4Mn(CaAlF)_3(PO_4)_3$ | 28·8 | — | 15·0 | — | 19·5 | — | — | — | 8·4 | 18·9 | 6·5 | — |
| Morinite | $Na_2(CaAl)_4(F_6O_2)(PO_4)_4,5H_2O$ | 33·0 | — | 5·1 | — | 13·6 | — | — | — | — | 17·5 | 13·0 | 17·6 |
| Jezekite | $Na_4CaAl_2(F.OH)_2(PO_4)_2.O$ | 30·3 | — | 18·7 | — | 13·5 | — | — | — | — | 21·9 | 8·2 | 7·3 |
| Brazilianite | $NaAl_3(OH)_4(PO_4)_2$ | 38·0–38·7 | — | 8·3 | — | — | — | — | — | — | 42·9–43·8 | — | 9·8 |
| Stercorite | $NaNH_4.H.PO_4,4H_2O$ | 34·4 | — | 3·1 | 7·7–8·5 | — | — | — | — | — | — | — | 42·3 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Na_2O$ | $K_2O$ | MgO | CaO | FeO | $Fe_2O_3$ | MnO | $Al_2O_3$ | F | $CO_2$ | $H_2O$ |
| Bradleyite | $Na_3MgCO_3PO_4$ | 28·3 | 37·6 | — | 15·4 | — | — | 0·6 | — | 0·3 | — | 18·4 | 0·4 |
| Griphite | $(NaCaFeAl)_6(MnF.OH)_4(PO_4)_5$ | 38·5–39·7 | 3·3–5·5 | — | — | 6–7·5 | 2–10·7 | 2·4–7·0 | 18–29·6 | 8·7–10·1 | 0–3·0 | — | 2·6–4·3 |
| Dehrnite | $(NaKCa)_5(CO_3)_3(PO_4)_3.OH$ | 35·7–37·1 | 3·7–7·1 | 0·3–5·9 | — | 47·7–54·9 | — | — | — | — | — | 1·2–3·3 | 1·7–3·0 |
| Lewistonite | $(CaNaK)_5(PO_4)_3.OH$ | 32·3–37·9 | 0·5–4·3 | 1·4–3·7 | — | 41·4–46·8 | — | — | — | — | — | — | 7·7–8·6 |
| Wardite | $Na(OH)_4Al_3(PO_4)_2,2H_2O$ | 34·7 | 6–7 | — | — | 0–3 | — | — | — | 36·6–38·3 | — | — | 17·9 |
| Millisite | $NaKCaAl_6(OH)_9(PO_4)_4,3H_2O$ | 33·8 | 2·8 | 1·7 | — | 7·1 | — | — | — | 36·3 | — | — | 18·0 |
| Lehiite | $Na_2K_2Ca_5Al_8(OH)_{12}(PO_4)_8,6H_2O$ | 34·6 | 2·7 | 2·3 | — | 18·1 | — | — | — | 27·8 | — | — | 14·2 |
| Leucophosphite | $KFe_2.OH(PO_4)_2,2H_2O$ | 27–34·7 | — | 8–10·9 | — | — | — | 37–41·0 | — | — | — | — | 11·2 |
| Englishite | $K_2Ca_4Al_8(OH)_{10}(PO_4)_8,9H_2O$ | 37·8 | — | 5·4 | — | 14·1 | — | — | — | 24·7 | — | — | 16·5 |
| Minyulite | $K_2Al_4(OH)_2(PO_4)_4,7H_2O$ | 35·6 | — | 12·3 | — | — | — | — | — | 30·0 | — | — | 20·6 |
| Taranakite | $(K,NH_4)_3H_6Al_5(PO_4)_8,18H_2O$ | 35·1–38·9 | — | 4·2–8·9 | — | 0·4–0·6 | — | 0·8–1·7 | — | 17·0–22·9 | — | — | 28·2–34·9 |

*Table XVI.—(continued)*

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Na_2O$ | $K_2O$ | BeO | CaO | FeO | $Fe_2O_3$ | MnO | $Al_2O_3$ | F | $CO_2$ | $H_2O$ |
| Beryllonite | $NaBePO_4$ | 55·6 | 23·5 | — | 19·4 | — | — | — | — | — | — | — | — |
| Monetite | $CaHPO_4$ | 52·2 | — | — | — | 41·0 | — | — | — | — | — | — | 6·6 |
| Brushite | $CaHPO_4.2H_2O$ | 38–42·7 | — | — | — | 30·8–33·0 | — | — | — | — | — | — | 23·3–30·9 |
| Whitlockite | $Ca_3(PO_4)_2$ | 45·7–45·9 | — | — | — | 46·8–48·2 | — | — | — | — | — | — | — |
| Isoclasite | $Ca_2.OH.PO_4,2H_2O$ | 29·9 | — | — | — | 49·5 | — | — | — | — | — | — | 20·6 |
| Graftonite | $(CaFeMn)_3(PO_4)_2$ | 38·9–41·7 | — | — | — | 4·5–12·8 | 27·8–32·6 | — | 15·7–25·5 | — | — | — | — |
| Francolite | $Ca_{10}(PO_4)_6F_2$ | 38·1–38·3 | — | — | — | 54·0–54·6 | — | — | — | — | 2·8–3·7 | 2·0–3·4 | — |
| Carbonate–apatite | $Ca_{10}(PO_4)_6CO_3,H_2O$ | 34·6–38·6 | — | — | — | 51·3–56·5 | — | — | — | — | 1·4–2·8 | 3·2–4·5 | 1·2–4·4 |
| Fluorapatite | $Ca_{10}(PO_4)_6F_2$ | 38·1–42·0 | — | — | — | 42·4–55·6 | — | — | — | — | 1·2–3·7 | 0–3·4 | 0–1·0 |
| Spodiosite | $Ca_2PO_4.F$ | 29·6–32·2 | — | — | — | 45·8–49·8 | — | 1–2·4 | — | — | 2·9–4·7 | 0–3·9 | — |
| Hydroxyapatite | $Ca_{10}(PO_4)_6(OH)_2$ | 38·6–42·2 | — | — | — | 44·1–55·8 | — | — | — | — | 0–1·0 | — | 1·2–2·9 |
| Herderite | $CaBePO_4.F$ | 43·4–44·3 | — | — | 15–15·8 | 33·4 | — | — | — | — | 8·9–11·3 | — | 0–1·0 |
| Hydroxyherderite | $CaBePO_4.F.OH$ | 39·7–44·1 | — | — | 15·5–16·5 | 32·2–34·0 | — | — | — | — | 0–5·3 | — | 3·7–8·0 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | MnO | FeO | $Fe_2O_3$ | MgO | $Al_2O_3$ | BeO | $SiO_2$ | $SO_3$ | F | $H_2O$ |
| Fairfieldite | $Ca_2MnFe(PO_4)_2,2H_2O$ | 37·7–39·6 | 28·9–30·9 | 12·4–19·7 | 1·0–7·0 | — | — | — | — | — | — | — | 9·7–10·0 |
| Collinsite | $Ca_2MgFe(PO_4)_2,2H_2O$ | 39·8–41·1 | 32·1 | — | 6·9–7·3 | — | 6·3–9·3 | — | — | — | — | — | 9·7–12·3 |
| Anapaite | $Ca_2Fe(PO_4)_2,4H_2O$ | 34·4–35·5 | 26·4–28·3 | — | 17·5–20·0 | — | — | — | — | — | — | — | 18·3–18·6 |
| Borickite | $CaFe_5(OH)_{11}(PO_4)_2,3H_2O$ | 19·4–20·5 | 7·3–8·2 | — | — | 52·3–53·0 | — | — | — | — | — | — | 19·1–20 |
| Foucherite | $Ca(FeAl)_4(OH)_8(PO_4)_2,7H_2O$ | 19·5 | 7·7 | — | — | 38·5 | — | 4·5 | — | — | — | — | 28·5 |
| Davisonite | $Ca_3Al(OH)_3(PO_4)_2,H_2O$ | 30·3–33·1 | 40·3–41·7 | — | — | — | 1·4–6·0 | 11·8–15·2 | — | — | — | — | 6·7–11·6 |
| Egueite | $CaFe_4(OH)_{14}(PO_4)_{10},21H_2O$ | 30·3 | 2–3 | — | — | 44·2 | — | 1·5 | — | — | — | — | 20·5 |
| Mitridatite | $CaFe_2(OH)_2(PO_4)_2,nH_2O$ | 17·2–30·6 | 8·2–16·1 | — | — | 29·0–43·3 | — | — | — | — | — | — | 13·1–26·8 |
| Richellite | $Ca_3Fe_{10}(OH)_{12}(PO_4)_8,nH_2O$ | 25·5–28·8 | 5·5–7·2 | — | — | 28·7–29·7 | — | — | — | — | — | — | 29·4–33·1 |
| Roscherite | $(CaMnFe)_3(BePO_4)_3(OH)_3,2H_2O$ | 38·0 | 11·5 | 14·5 | 10·1 | — | — | — | 13·7 | — | — | — | 12·2 |
| Calcioferrite | $Ca_3Fe_3(OH)_3(PO_4)_4,8H_2O$ | 34·0 | 14·8 | — | — | 24·3 | — | — | — | — | — | — | 20·6 |
| Xanthoxenite | $Ca_2FeOH(PO_4)_2,1\frac{1}{2}H_2O$ | 37·6 | 25·0 | 4·6 | — | 21·7 | — | — | — | — | — | — | 10·0 |
| Montgomeryite | $Ca_4(AlOH)_5(PO_4)_6,11H_2O$ | 37·7 | 19·0 | — | — | — | — | 21·4 | — | — | — | — | 21·7 |
| Overite | $Ca_3Al_8(OH)_6(PO_4)_8,15H_2O$ | 37·9 | 11·6 | — | — | — | — | 28·0 | — | — | — | — | 22·0 |
| Crandallite | $CaAl_3(OH)_5(PO_4)_2,H_2O$ | 25·2–35·6 | 7·5–16·9 | — | — | — | — | 28·2–38·8 | — | — | — | — | 17·4–20·0 |
| Deltaite | $CaAl_2Mg(OH)_4(PO_4)_2,H_2O$ | 27·6–33·4 | 23–24·4 | — | — | — | 0–3·4 | 26·9–29·4 | — | — | — | — | 13·1–14·3 |
| Kolbeckite | $CaBeAlSiPO_4$ | 33·8 | 3·2 | — | — | — | — | 21·4 | 8·7 | 9·3 | — | — | 23·5 |
| Wilkeite | $Ca_5(OH,F)(PO_4.SO_4.SiO_4)_3$ | 14·4–32·2 | 54·4 | — | — | — | — | — | — | 2·9–11·2 | 12·3 | 0–2·1 | — |
| Woodhouseite | $CaAl_3(OH)_6PO_4.SO_4$ | 18·1 | 12·3 | — | — | — | — | 36·6 | — | — | 17·6 | — | 13·5 |
| Ardealite | $Ca_2HPO_4.SO_4,4H_2O$ | 21·9–23·5 | 31·6–32·1 | — | — | — | — | — | — | — | 21·3–23·1 | — | 25·1 |
| Cirrolite | $Ca_3Al_2(OH)_3(PO_4)_3$ | 41·2 | 29·4 | 2·2 | 0·9 | — | — | 20·5 | — | — | — | — | 5·1 |
| Calcium ferric phosphate | $2CaO.3Fe_2O_3.2P_2O_5,10H_2O$ | 22·7 | 8·2 | — | — | 29·0 | — | 2·7 | — | — | — | — | 13·5 |
| Messelite | $(Ca,Fe,Mn,Mg)_3(PO_4)_2,3H_2O$ | 37·7 | 31·1 | 0–7·2 | 14–15·6 | — | 1·5 | — | — | — | — | — | 12·2 |

## Table XVI.—(continued)

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | MnO | MgO | FeO | $Al_2O_3$ | $SO_3$ | $SiO_2$ | Cl | $CO_2$ | F | $H_2O$ |
| Triplite | $(CaMnFeMg)_2.PO_4.F.OH$ | 31·8–33·1 | 2·2–3·2 | 37·4–57·6 | 0·6–1·3 | 1·7–21·9 | — | — | — | — | — | 7·6–9·1 | 0·5 |
| Sarcopside | $(Fe,Mn,Mg)_3(PO_4)_2$ | 33·3–39·7 | — | 6·2–6·9 | 2·7–3·5 | 50–51·3 | — | — | — | — | — | — | — |
| Dahllite | $3Ca_3(PO_4)_2.CaO.CO_3,nH_2O$ | 38·4 | 53·0 | — | — | — | — | — | — | — | 6·3 | — | 1·4 |
| Tavistockite | $Ca_3Al_2(OH)_3(PO_4)_3$ | 30·4 | 36·3 | — | — | — | 22·4 | — | — | — | — | — | 12·0 |
| Baldaufite | $(CaMgFeMn)_5.H_2(PO_4)_4,5H_2O$ | 39·1 | 6·2 | 9·3 | 2·7 | 27·1 | — | — | — | — | — | — | 15·6 |
| Ellestadite | $Ca_5(PO_4.SO_4.CO_4.SiO_4)_3F.Cl.OH$ | 3·1 | 55·2 | — | — | — | — | 20·7 | 17·3 | 1·7 | 0·6 | 0·6 | 1·0 |
| Chlorapatite | $Ca_{10}(PO_4)_6Cl_2$ | 40·5 | 53·0 | — | 0–1·0 | — | — | — | — | 4·1 | — | 0·2 | 0·2–1·0 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | SrO | BaO | $As_2O_5$ | PbO | $Al_2O_3$ | $SO_3$ | MgO | Cl | F | $H_2O$ |
| Fermorite | $(CaSr)_5(PO_4AsO_4)_3.F.OH$ | 20·1 | 44·3 | 10·0 | — | 25·2 | — | — | — | — | — | 0·8 | 1·4 |
| Svabite | $(CaPb)_5(PO_4AsO_4)_3F.Cl.OH$ | 0–12·5 | 37·2–45·5 | — | — | 35·2–52·2 | 0–4·5 | — | — | — | 0–0·5 | 1·4–2·8 | 0·3–2·3 |
| Goyazite | $SrAl_3(OH)_5(PO_4)_2,H_2O$ | 14·9–31 | — | 17·3–19·8 | 0–4·0 | — | — | 32·3–50·7 | — | — | — | — | 12–16·7 |
| Gorceixite | $BaAl_3(OH)_5(PO_4)_2,H_2O$ | 21·5–24·1 | 0–3·6 | — | 11·9–26·0 | — | — | 34·6–38·0 | — | — | — | — | 14·6–15·3 |
| Svanbergite | $SrAl_3(OH)_6PO_4.SO_4$ | 16·7–21·2 | — | 12·8–18·0 | — | — | — | 32·7–37·0 | 11·5–17·3 | — | — | — | 11·6–12·5 |
| Hinsdalite | $SrPbAl_3(OH)_6PO_4.SO_4$ | 14·5 | — | 3·1 | — | — | 31·8 | 26·5 | 14·1 | — | — | — | 10·3 |
| Newberyite | $MgHPO_4,3H_2O$ | 40·7 | — | — | — | — | — | — | — | 22·4 | — | — | 35·8 |
| Phosphorroesslerite | $MgHPO_4,7H_2O$ | 28·1 | — | — | — | — | — | — | — | 16·3 | — | — | 54·5 |
| Bobierrite | $Mg_3(PO_4)_2,8H_2O$ | 34·5 | — | — | — | — | — | — | — | 25·0–30 | — | — | 34·3–35·4 |
| Wagnerite | $Mg_2PO_4.F$ | 40·2–43·4 | 2·5–13·5 | — | — | — | — | — | — | 37·6–48·3 | — | 5·1–11·5 | — |
| Gordonite | $MgAl_2(OH)_2(PO_4)_2,8H_2O$ | 32·8 | — | — | — | — | — | 20·7 | — | 10·0 | — | — | 35·0 |

*Table XVI.—(continued)*

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $MgO$ | $(NH_4)_2O$ | $FeO$ | $Al_2O_3$ | $Fe_2O_3$ | $ZnO$ | $MnO$ | $CuO$ | $CaO$ | $Cl$ | $H_2O$ |
| Schertelite | $Mg(NH_4)_2H_2(PO_4)_2,4H_2O$ | 43·9 | 12·2 | 16·2 | — | — | — | — | — | — | — | — | 27·6 |
| Hannayite | $Mg_3(NH_4)_2(HPO_4)_4,8H_2O$ | 44·6–45·7 | 18·4–18·9 | 8·1 | — | — | — | — | — | — | — | — | 28·4 |
| Struvite | $MgNH_4PO_4,6H_2O$ | 28·1–28·8 | 13·2–16·6 | 11·0–11·8 | — | — | — | — | — | — | — | — | 43·6–44 |
| Lazulite | $MgFeAl_2(OH)_2(PO_4)_2$ | 44·3–46·1 | 8–12 | — | 2·8–8·9 | 30·9–32·6 | — | — | — | — | — | — | 5·8–6·5 |
| Scorzalite | $MgFeAl_2(OH)_2(PO_4)_2$ | 42·8 | 3–4·2 | — | 14·7–17·1 | 30·8 | — | — | — | — | — | — | 5·9–6·1 |
| Souzalite | $(MgFe)_3(AlFe)_4(OH)_6(PO_4)_4,2H_2O$ | 37·7 | 9·6 | — | 11·5 | 26·1 | 2·7 | — | — | — | — | — | 12·0 |
| Hopeite | $Zn_3(PO_4)_2,4H_2O$ | 31·8 | — | — | — | — | — | 52·0 | — | — | — | — | 16·1 |
| Parahopeite | $Zn_3(PO_4)_2,4H_2O$ | 30·5–31·6 | — | — | — | — | — | 53·0–54·7 | — | — | — | — | 15·3–15·6 |
| Hibbenite | $Zn_7(OH)_2(PO_4)_4,7H_2O$ | 28·8 | — | — | — | — | — | 57·6 | — | — | — | — | 13·7 |
| Phosphophyllite | $Zn_2FeMn(PO_4)_2,4H_2O$ | 32·5 | — | — | 12·2 | — | — | 34·3 | 5·0 | — | — | — | 16·5 |
| Tarbuttite | $Zn_2(OH)PO_4$ | 29·2 | — | — | — | — | — | 66·6 | — | — | — | — | 3·8 |
| Spencerite | $Zn_4(OH)_2(PO_4)_2,3H_2O$ | 26·2 | — | — | — | — | — | 60·3 | — | — | — | — | 13·4 |
| Turquoise | $Cu(AlFe)_6(OH)_8(PO_4)_4,4H_2O$ | 30·4–34·4 | — | — | — | 20·8–44·8 | 0–4·4 | — | — | 7·4–9·0 | — | — | 11·9–20·2 |
| Chalcosiderite | $Cu(AlFe)_6(OH)_8(PO_4)_4,4H_2O$ | 28·6–33·8 | — | — | — | 4·5–20·8 | 21·3–42·8 | — | — | 6·8–8·2 | — | — | 11·9–16·5 |
| Cornetite | $(CuOH)_3PO_4$ | 19·8 | — | — | — | — | — | — | — | 70·8 | — | — | 9·4 |
| Pseudo-malachite | $Cu_5(OH)_4(PO_4)_2,H_2O$ | 20–23·9 | — | — | — | — | — | — | — | 67–71·4 | — | — | 6·8–8·5 |
| Libethenite | $Cu_2OHPO_4$ | 26·5–29·3 | — | — | — | — | — | — | — | 66·6 | — | — | 3·7–4 |
| Veszelyite | $(CuZnOH)_3PO_4,2H_2O$ | 18·4–19·9 | — | — | — | — | — | 23·6–28·9 | — | 36·0–40·4 | — | — | 14·3–16·9 |
| Tagilite | $Cu_2OHPO_4,H_2O$ | 26·4–27·3 | — | — | — | — | — | — | — | 61·3–62·4 | — | — | 10·3–10·8 |
| Andrewsite | $(CuFe)_3Fe_6(OH)_{12}(PO_4)_4$ | 26·1 | — | — | 7·1–8·6 | — | 43–44·6 | — | — | 10·9 | — | — | 8·8 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Na_2O$ | $(NH_4)_2O$ | $FeO$ | $Al_2O_3$ | $Fe_2O_3$ | $ZnO$ | $MnO$ | $CuO$ | $CaO$ | $Cl$ | $H_2O$ |
| Sampleite | $Cu_5CaNa(PO_4)_4Cl,5H_2O$ | 32·1 | 3·1–3·5 | — | — | — | — | — | — | 44·1 | 5·8 | 4·0 | 9·7 |
| Kehoeite | $Al_8(Ca,Zn)_3(PO_4)_6(OH)_{12},21H_2O$ | 27·0 | — | — | — | 24·8 | — | 14·6 | — | — | 2·7 | — | 31·1 |
| Richmondite | $AlPO_4,4H_2O$ | 37·6 | — | — | — | 26·7 | — | — | — | — | — | — | 35·7 |
| Callainite | $AlPO_4,2\frac{1}{2}H_2O$ | 42·6 | — | — | — | 29·6 | 1·8 | — | — | — | — | — | 23·6 |
| Fischerite | $AlOHPO_4,H_2O$ | 29·0–35·3 | — | — | — | 34·5–37·2 | — | — | — | — | — | — | 27·5 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Na_2O$ | $SrO$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $ZnO$ | $MnO$ | $CuO$ | $CaO$ | $Cl$ | $H_2O$ |
| Attacolite | $(Ca,Sr,Mn)_3(Al,Fe,Mn)_8(PO_4,SiO_2)_{7-m}(OH)_{4m},3H_2O$ | 32·6–36·1 | — | 0–3·3 | 0–9·4 | 27–29·8 | 0–4·0 | — | 7·1–8·0 | — | 11·4–13·2 | — | 5·9–6·9 |
| Trolleite | $Al_4(OH,PO_4)_3$ | 46·7 | — | — | — | 43·3 | 2·75 | — | — | — | 1·0 | — | 6·2 |

*Table XVI.—(continued)*

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Al_2O_3$ | $Fe_2O_3$ | FeO | $Na_2O$ | $SO_3$ | MnO | MgO | $B_2O_3$ | PbO | F | $H_2O$ |
| Berlinite | $AlPO_4$ | 58·2 | 41·8 | — | — | — | — | — | — | — | — | — | — |
| Variscite | $AlPO_4,2H_2O$ | 41·2–45·0 | 16·6–32·4 | — | — | — | — | — | — | — | — | — | 22·7–26·0 |
| Augelite | $Al_2(OH)_3PO_4$ | 34·6–35·5 | 49·1–51·4 | — | — | — | — | — | — | — | — | — | 12·9–13·9 |
| Meyersite | $(AlFe)PO_4,2H_2O$ | 28·9 | 31·8 | 1·3 | — | — | — | — | — | — | — | — | 26·1 |
| Evansite | $Al_3(OH)_6PO_4,6H_2O$ | 18·0–21·7 | 34·5–40·2 | — | — | — | — | — | — | — | — | — | 37·0–41·5 |
| Harbortite | $Al_3(OH)_3(PO_4)_2,3H_2O$ | 34·1–35·7 | 33·1 | 3·8–5·1 | — | 3·7–4·7 | — | — | — | — | — | — | 18·3 |
| Coeruleolactite | $Al_3(OH)_3(PO_4)_2,4H_2O$ | 36·3 | 35·1–38·3 | — | — | — | — | — | — | — | — | — | 21·5 |
| Wavellite | $Al_3(OH)_3(PO_4)_2,5H_2O$ | 32·7–34·2 | 31·1–37·4 | 0–3·2 | — | — | — | — | — | — | — | 0–2·8 | 26·5–28·6 |
| Sterrettite | $Al_6(OH)_6(PO_4)_4,5H_2O$ | 40·1 | 39·1 | — | — | — | — | — | — | — | — | — | 20·4 |
| Vashegyite | $Al_4(OH)_3(PO_4)_3,nH_2O$ | 26·6–31·3 | 26·5–28·3 | — | — | — | — | — | — | — | — | — | 39·0–44·7 |
| Vauxite | $Al_2Fe(PO_4)_2,7H_2O$ | 30·4 | 21·4–23·8 | — | 15·3 | — | — | — | — | — | — | — | 30·6–31·6 |
| Metavauxite | $Al_2Fe(OH)_2(PO_4)_2,8H_2O$ | 28·5–29·5 | 17·4–21·0 | — | 14·6–17·0 | — | — | — | — | — | — | — | 33·2–35·0 |
| Paravauxite | $Al_2Fe(OH)_2(PO_4)_2,8H_2O$ | 27·6–29·8 | 21·3 | — | 13·7 | — | — | — | — | — | — | — | 34·1–35·7 |
| Kribergite | $Al_{16}(OH)_{18}(SO_4)_3(PO_4)_8,10H_2O$ | 31·3 | 38·5 | — | — | — | 13·1 | — | — | — | — | — | 17·2 |
| Childrenite | $AlFeMn(OH)_2(PO_4),H_2O$ | 29·9–30·7 | 15·9–21·4 | — | 21·7–28·6 | — | — | 3·1–7·7 | — | — | — | — | 15·8–17·1 |
| Eosphorite | $AlFeMn(OH)_2(PO_4),H_2O$ | 29·9–31·0 | 20·5–22·4 | — | 1·4–7·4 | — | — | 23·5–29·9 | — | — | — | — | 15·4 |
| Lueneburgite | $B_2Mg_3(OH)_6(PO_4)_2,6H_2O$ | 29·7 | — | — | — | — | — | — | 25·2 | 12·8 | — | — | 32·2 |
| Seamanite | $BO_3Mn_3PO_4,3H_2O$ | 15·9 | — | — | — | — | — | 56·4 | 1·3 | 9·9 | — | — | 14·6 |
| Corkite | $PbFe_3(OH)_6SO_4.PO_4$ | 9·0–9·5 | — | 34·6–40·7 | — | — | 12·7–13·8 | — | — | — | 24·0–32·3 | — | 8·5–9·8 |
| Plumbogummite | $PbAl_3(OH)_5(PO_4)_2,H_2O$ | 17·6–22·3 | 21·0–29·5 | — | — | — | — | — | — | — | 34·4–38·9 | — | 14·7–16·2 |
| Meta–variscite | $AlPO_4,2H_2O$ | 44·7 | 32·4 | — | — | — | — | — | — | — | — | — | 22·7 |
| Redondite | $FeAlPO_4,2H_2O$ | 40·7–42·5 | 29·3–34·7 | 0·3–3·5 | — | — | — | — | — | — | — | — | 16·8–22·7 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $As_2O_5$ | PbO | CuO | CaO | $Fe_2O_3$ | $Al_2O_3$ | FeO | MnO | $V_2O_5$ | Cl | $H_2O$ |
| Liroconite | $Cu_2Al(AsO_4,PO_4)(OH)_4,4H_2O$ | 3·5–3·7 | 22·2–26·5 | — | 36·4–37·2 | — | — | 9·7–11·8 | — | — | — | — | 24·9–25·5 |
| Pyromorphite | $Pb_5(PO_4AsO_4)_3Cl$ | 8·3–19·8 | 0–11·3 | 52·6–81·3 | — | 0–12·3 | — | — | — | — | — | 1·7–2·9 | — |
| Calcium pyromorphite | $(Ca,Pb)_5(PO_4,AsO_4)_3Cl$ | 1·9–19·8 | 4–26 | 5·26–71·3 | 0–2 | 2·8–12·3 | — | — | — | — | 0–6 | 2–3 | — |
| Collieite | $(Pb,Cu)_5(PO_4,VO_4)_3Cl$ | 16·3 | — | 66·8 | 1·2 | 8·6 | — | — | — | — | 4·1 | 2·8 | — |
| Mimetite | $Pb_5(AsO_4PO_4)_3Cl$ | 0·3–5·4 | 12·1–26·0 | 66·8–75·1 | — | 0–8·3 | — | — | — | — | — | 2·4 | — |
| Tsumebite | $Pb_2Cu(OH)_3PO_4,3H_2O$ | 10·3–12·0 | — | 63·8–65·1 | 11·8–12·1 | — | — | — | — | — | — | — | 12·1–12·7 |
| Strengite | $FePO_4,2H_2O$ | 37·6–38·9 | — | — | — | — | 26·1–43·4 | 0–12·5 | — | — | — | — | 18·9–21·6 |
| Meta-strengite | $FePO_4,2H_2O$ | 37·7–38·9 | — | — | — | — | 44·3 | — | — | — | — | — | 17·3 |
| Koninckite | $FePO_4,3H_2O$ | 34·8 | — | — | — | — | 34·4 | 4·6 | — | — | — | — | 26·2 |
| Vivianite | $Fe_3(PO_4)_2,8H_2O$ | 27·0–30·0 | — | — | — | — | 0–41·8 | — | 9·5–39·1 | — | — | — | 25–28·8 |
| Laubmannite | $Fe_9(OH)_{12}(PO_4)_4$ | 26·0 | — | — | — | — | 43·0–57·9 | — | 2·0–19·7 | — | — | — | 8·4–10·1 |
| Tinticite | $(FeOH)_3(PO_4)_2,3\frac{1}{2}H_2O$ | 28·4–30·2 | — | — | — | — | 49·0 | — | — | — | — | — | 19–19·7 |
| Cacoxenite | $Fe_4(OH)_3(PO_4)_3,12H_2O$ | 19·8–26·8 | — | — | — | — | 40·4–48·6 | — | — | — | — | — | 30·6–32·8 |
| Beraunite | $Fe_5(OH)_5(PO_4)_3,3H_2O$ | 27·2–31·8 | — | — | — | — | 49·6–56·0 | — | 0–2·0 | — | — | — | 13·5–16·6 |
| Dufrenite | $Fe_5(OH)_5(PO_4)_3,2H_2O$ | 30·3–31·8 | — | — | — | — | 40·2–60·2 | — | 1·5–8·3 | — | — | — | 8·0–14·4 |
| Delvauxite | $Fe_4(OH)_6(PO_4)_2,nH_2O$ | 16·0–24·5 | — | — | — | — | 34·2–46·5 | — | — | — | — | — | 28·0–50·0 |

*Table XVI.—(continued)*

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $As_2O_5$ | PbO | CuO | CaO | $Fe_2O_3$ | $Al_2O_3$ | FeO | MnO | $SO_3$ | Cl | $H_2O$ |
| Diadochite | $Fe_2(OH)PO_4SO_4,5H_2O$ | 14·8–19·2 | — | — | — | — | 35·1–39·7 | — | — | — | 10·9–19·3 | — | 25·7–34·5 |
| Barrandite | $(Fe,Al)PO_4,2H_2O$ | 38·9 | — | — | — | — | 26·1 | 12·5 | — | — | — | — | 20·6 |
| Bosphorite | $(Fe,Mn)_3(PO_4)_2.OH,7H_2O$ | 28·0 | — | — | — | — | 41·8 | — | — | 2·6 | — | — | 25·0 |
| Triploidite | $(FeMn)_2(OH)PO_4$ | 30·9–32·6 | — | — | — | 0·3–1 | 0–4·3 | — | 14·9–24·3 | 29·9–48·5 | — | — | 4·1 |
| Wolfeite | $(FeMn)_2(OH)PO_4$ | 32·4–34·2 | — | — | — | 0·2–2·0 | 0·2–7·8 | — | 33·4–44·4 | 13·1–21·7 | — | — | 3·8–4·4 |
| Heterosite | $FeMnPO_4$ | 38·7–43·8 | — | — | — | — | 27·4–38·4 | — | — | 12·1–24·5 | — | — | — |
| Purpurite | $FeMnPO_4$ | 41·6–47·3 | — | — | — | — | 15·9–24·6 | — | — | 29·3 | — | — | — |
| Reddingite | $(FeMn)_3(PO_4)_2,3H_2O$ | 34·5–35·2 | — | — | — | — | — | — | 2·2–17·1 | 34·5–48·2 | — | — | 12·3–13·3 |
| Phosphoferrite | $(FeMn)_3(PO_4)_2,3H_2O$ | 34·5 | — | — | — | — | — | — | 37·5 | 13·6 | — | — | 13·1 |
| Landesite | $Fe_6Mn_{20}(PO_4)_{16},27H_2O$ | 31·9 | — | — | — | — | 13·9 | — | — | 33·7 | — | — | 13·6 |
| Salmonsite | $Fe_2Mn_9(PO_4)_8,14H_2O$ | 34·9 | — | — | — | — | 9·5 | — | — | 37·7 | — | — | 15·3 |
| Frondelite | $Fe_5Mn(OH)_5(PO_4)_3$ | 31·4 | — | — | — | — | 48·9–55·2 | — | — | 4·1–7·7 | — | — | 7·3 |
| Asovskite | $Fe_3(OH)_6PO_4$ | 15·9–17·0 | — | — | — | — | 52·7–57·2 | — | — | 0–1·7 | — | — | 23·2–25·8 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | MnO | FeO | MgO | $Fe_2O_3$ | $Mn_2O_3$ | CaO | $UO_3$ | BaO | PbO | CuO | $H_2O$ |
| Hureaulite | $Mn_5H_2(PO_4)_4,4H_2O$ | 38·2 | 32·9–42·3 | 4·6–11·1 | — | — | — | — | — | — | — | — | 12–18 |
| Wenzelite | $(MnFeMg)H_2PO_4,2H_2O$ | 38·9–39·4 | 21·1–23·9 | 6·0 | 6·8 | — | — | — | — | — | — | — | 23·5 |
| Rockbridgeite | $MnFe_5(OH)_5(PO_4)_3$ | 30·4–42·8 | 0–3·7 | 1–6·1 | — | 50·8–55·8 | — | — | — | — | — | — | — |
| Ludlamite | $(MnFeMg)_3(PO_4)_2,4H_2O$ | 30·1–33·9 | 0–3·1 | 45·9–52·8 | 0–2·2 | — | — | — | — | — | — | — | 14·9–17·0 |
| Bermanite | $Mn_{13}Fe_8Mg_5(OH)_{10}(PO_4)_8,15H_2O$ | 31·4 | 13·8 | — | 2·4 | 3·0 | 28·8 | — | — | — | — | — | 19·3 |
| Autunite | $CaUO_2(PO_4)_2,10–12H_2O$ | 13·4–15·2 | — | — | — | — | — | 5·3–6·6 | 58·9–61·7 | — | — | — | 14·9–20·3 |
| Uranocircite | $Ba(UO_2PO_4)_2,8H_2O$ | 15·1 | — | — | — | — | — | — | 56·9 | 14·6 | — | — | 14·0 |
| Saléeite | $Mg(UO_2PO_4)_2,10H_2O$ | 12·0–15·2 | — | — | 4·3–5·0 | — | — | — | 60·3–64·1 | — | — | — | 16·5–19·3 |
| Parsonsite | $Pb_2UO_2(PO_4)_2,2H_2O$ | 14·5–15·1 | — | — | — | — | — | — | 29·7–34·7 | — | 44·7–47·4 | — | 1·6–3·4 |
| Renardite | $Pb(OH)_4(UO_2)_4(PO_4)_2,7H_2O$ | 8·2–8·7 | — | — | — | — | — | — | 64·8–69·0 | — | 12·3–13·0 | — | 8·7–9·3 |
| Dumontite | $Pb_2(UO_2)_3(OH)_4(PO_4)_2,5H_2O$ | 8·7 | — | — | — | — | — | — | 56·5 | — | 27·2 | — | 5·8 |
| Phosphuranylite | $Ca(OH)_4(UO_2)_4(PO_4)_2,7H_2O$ | 9·8–12·1 | — | — | — | — | — | 3·8 | 76·7 | — | — | — | 10·8–11·2 |
| Dewindtite | $Pb_3(UO_2)_6(OH)_6(PO_4)_4,9H_2O$ | 10·4 | — | — | — | — | — | — | 54·8–56·1 | — | 24·9–26·2 | — | 6·7–8·1 |
| Torbernite | $(UO_2)_2Cu(PO_4)_2,8–12H_2O$ | 13·5–14·5 | — | 57–60·7 | — | — | — | — | — | — | — | 7·2–8·6 | 14·3–20·3 |
| Metatorbernite | $(UO_2)_2Cu(PO_4)_2,8H_2O$ | 13·4–14·0 | — | 58·8–59·7 | — | — | — | — | — | — | — | 8·5–11·4 | 13·6–15·0 |

Table XVI.—(continued)

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Y_2O_3$ | $UO_3$ | $SiO_2$ | $ThO_2$ | $Ce_2O_3$ | $La_2O_3$ | CaO | CuO | PbO | $CrO_3$ | $H_2O$ |
| Xenotime | $YPO_4$ | 25·4–36·0 | 51·8–67·8 | 0–5·1 | 0–4·3 | — | — | — | — | — | — | — | — |
| Monazite | $(Ce,La,Y,Th)PO_4$ | 24·9–29·7 | 0–5·1 | — | — | 0–12·0 | 21·1–32·3 | 27·9–41·8 | — | — | — | — | — |
| Churchite | $(Y,Ce,La)PO_4,2H_2O$ | 28·5–31·1 | 41·4 | — | — | — | 1·1 | 8·0 | — | — | — | — | 14·9–15·3 |
| Abukumalite | $CaY_2(SiO_4.PO_4)_2$ | 5·8 | 46·0 | — | 20·8 | 0·9 | 6·5 | — | 13·5 | — | — | — | — |
| Vauquelinite | $(CuPb)_5.CrO_4(PO_4)_2$ | 0–10 | — | — | — | — | — | 4·6–12·4 | — | 4·6–12·4 | 61·0–71·0 | 10·0–27·0 | 1·0–3·0 |
| Rhabdophane | $(Ce,Y,La,Dy)PO_4,H_2O$ | 24·8 | 0–8·7 | — | — | — | 0–61·7 | 0–55·0 | — | — | — | — | 7·4 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Al_2O_3$ | $Ce_2O_3$ | $Na_2O$ | CaO | $ThO_2$ | $SiO_2$ | $R_2O_3$ | $As_2O_5$ | $V_2O_4$ | F | $H_2O$ |
| Florencite | $CeAl_3(OH)_6(PO_4)_2$ | 25·6–27·0 | 30·8–32·3 | 28·0–29·3 | — | — | — | — | — | — | — | — | 11·0 |
| Auerlite | $Th_3(SiO_4)_3(PO_4)_2,6H_2O$ | 7·5–8·6 | — | — | — | — | 70–72 | 6·8–7·6 | — | — | — | — | 10·6–11·2 |
| Britholite | $(Ca,Th,Ce)_5(PO_4,SiO_4)_3F,OH$ | 1·9–17·0 | 0–14·9 | — | — | 11·5–28·8 | 3·2–9·8 | 12·3–22·0 | 27·6–57 | — | — | 1·4–2·1 | 0–6·4 |
| Sincosite | $Ca.V_2O_2.(PO_4)_2,5H_2O$ | 31·1–31·7 | — | — | — | 12·1–13·3 | — | — | — | — | 36·3–37·8 | — | 17·1–19·9 |
| Viséite | $Na_2Ca_{10}[(Al_{20}Si_6P_{10}H_{36})O_{46}],16H_2O$ | 20·5 | 26·2 | — | 1·8 | 14·8 | — | 9·9 | — | — | — | 0·7 | 26·1 |

| Name | Formula | Percentage Composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Li_2O$ | $Na_2O$ | SrO | $Al_2O_3$ | $(NH_4)_2O$ | $Fe_2O_3$ | MnO | $TiO_2$ | CaO | $UO_3$ | $H_2O$ |
| Lithiophosphatite[305–6] | $Li_3PO_4$ | 59·9 | 37·1 | — | — | — | — | — | — | — | — | — | — |
| Palermoite[406, 307–8] | $(Li,Na)_2(Ca,Sr)(Al,OH)PO_4$ | 42·9–46·4 | 3·7–4·0 | 1·3–1·6 | 9·2–12·9 | 30·8–33·9 | — | — | — | — | 0·9–1·4 | — | — |
| Tavorite[315] | $(Li,Fe,Mn).PO_4,H_2O$ | 39·8 | 7·6 | — | — | — | — | 42·6 | 1·5 | — | — | — | 5·8 |
| Sodium autunite[334–5] | $NaUO_2.PO_4,4H_2O$ | 14·7 | — | 6·9 | — | — | — | — | — | — | — | 62·5 | 14·8 |
| Uramplite[333] | $NH_4UO_2.PO_4,3H_2O$ | 15·8 | — | — | — | — | 6·6 | — | — | — | — | 68·7 | 11·0 |
| Cyrilovite[265–8] | $NaFe_3(OH)_4.(PO_4)_2,2H_2O$ | 29·3 | — | 4·7 | — | 1·4 | — | 48·3 | 1·0 | — | — | — | 14·6 |
| Sabugalite[317] | $HAl(UO_2)_4(PO_4)_4,16H_2O$ | 16·1 | — | — | — | 2·7 | — | — | — | — | — | 65·2 | 15·9 |
| Lusungite[409] | $(Sr,Pb)Fe_3(PO_4)_2(OH)_2,H_2O$ | — | — | — | — | — | — | — | — | — | — | — | — |

| Name | Formula | Percentage composition | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Na_2O$ | $Fe_2O_3$ | CaO | CuO | ZnO | $Al_2O_3$ | $UO_3$ | $As_2O_5$ | $SiO_2$ | $H_2O$ |
| Chinoite[338] | $Cu_5(OH)_4(PO_4)_2$ | 24·3 | — | — | — | 69·1 | — | — | — | — | — | 6·6 |
| Uranospathite[322] | $Cu(UO_2)_2(AsO_4.PO_4)_2,11H_2O$ | 4·4 | — | — | — | 6·7 | — | — | 56·2 | 13·8 | — | 18·0 |
| Faustite[339] | $CuZn_4Al_{30}(OH)_{40}.(PO_4)_{20},25H_2O$ | 34·8 | — | — | — | 1·6 | 7·7 | 35·3 | — | — | — | 18·8 |
| Kamiokalite[346] | $(Cu,Zn)_3(PO_4)_2,7H_2O$ | 18·0 | — | — | — | 30·5 | 32·4 | — | — | — | — | 17·3 |
| Sodium uranospinite[320] | $Na_2CaO(UO_2)_2(AsO_4.PO_4)_2,5H_2O$ | 1·7 | 3·9 | 0·6 | 1·9 | — | — | 0·9 | 58·3 | 20·8 | 2·4 | 9·7 |

*Table XVI.—(continued)*

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Na_2O$ | BeO | CaO | CuO | MgO | FeO | MnO | $Fe_2O_3$ | F | $NO_3$ | $H_2O$ |
| Likasite$^{348}$ | $Cu_6(OH)_7(NO_3)_2(PO_4)_2$ | 14·6 | — | — | — | 55·5 | — | — | — | — | — | 15·1 | 16·5 |
| Isokite$^{349}$ | $CaMgPO_4F$ | 37·4 | — | — | 29·6 | — | 21·2 | — | — | — | 9·5 | — | — |
| Neomesselite$^{347}$ | $(CaFeMn)_3(PO_4)_2,2H_2O$ | 36·9 | — | — | 23·2–28·0 | — | — | 11·5–21·0 | 3·9–7·4 | — | — | — | 11·3 |
| Magniotriplite$^{416}$ | $(Mg,Fe,Mn)_2PO_4F$ | 30·6–33·3 | — | — | — | — | 17·1 | 25·9 | 13·0 | — | 6·0–9·0 | — | — |
| Glucine$^{410}$ | $Ca(Be,OH)_4(PO_4)_2,0{\cdot}5H_2O$ | 36·6–38·3 | — | 30·0–31·7 | 13·7–14·6 | — | — | — | — | — | — | — | 14·2–14·7 |
| Uralolite$^{411}$ | $CaBe_3(OH.PO_4)_2,4H_2O$ | 38·4–39·0 | — | 18·9–19·6 | 16·5–19·1 | — | — | — | — | — | — | — | 21·9–23·6 |
| Manganoan apatite$^{412}$ | $(Ca,Mn)_{10}(PO_4)_6F_2$ | 39·6–41·0 | 0·2–1·5 | — | 54·2–54·6 | — | — | — | 0–1·4 | — | 0–3·1 | — | — |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Na_2O$ | BeO | CaO | CuO | MgO | FeO | MnO | $Fe_2O_3$ | $UO_3$ | ZnO | $H_2O$ |
| Scholzite$^{325, 326}$ | $Ca_6Zn_2(OH)_4(PO_4)_4,2H_2O$ | 36·0 | — | — | 14·3 | — | 1·0 | 0·4 | 1·4 | — | — | 35·7 | 10·4 |
| Hurlbutite$^{316, 319}$ | $CaBe_2(PO_4)_2$ | 52·0–56·2 | 1·5 | 19·4–21·3 | 21·7 | — | — | — | — | — | — | — | 2·9 |
| Vayrynenite$^{330}$ | $(BeMnFe)OHPO_4$ | 40·4 | 1·4 | 12·1–13·9 | 1·8 | — | — | — | 30·6–34·0 | 6·6 | — | — | 5·0 |
| Faheyite$^{329}$ | $NaMnMgBe_2Fe_2(PO_4)_4,6H_2O$ | 38·1 | 0·8 | 7·3 | — | — | 1·1 | — | 6·0 | 21·4 | — | — | 14·9 |
| Moraesite$^{332}$ | $Be_2.OH.PO_4,4H_2O$ | 34·8 | — | 25·3 | — | — | — | — | — | — | — | — | 39·8 |
| Calcium hureaulite$^{316}$ | $CaMn_5(PO_4)_4,4H_2O$ | 36·4 | 2·9 | — | 8·6 | — | — | — | 38·9 | — | — | — | 10·0 |
| Kryzhanovskite$^{351}$ | $(Ca,Mg,Mn)O.Fe_2.(PO_4)_2,2H_2O$ | 35·3 | — | — | 1·5 | — | 1·3 | — | 16·4 | 34·6 | — | — | 8·8 |
| Hagendorfite$^{341}$ | $Na,Ca(MnFe)_2(PO_4)_2$ | 42·0 | 8·5–9·7 | — | 1·4–1·7 | — | 0·7–2·6 | 15·4–18·2 | 9·8–18·5 | 13·3–14·5 | — | — | 1·0 |
| Farringtonite$^{353}$ | $Mg_3(PO_4)_2$ | 37·6–50·0 | — | — | — | — | 41·6–49·0 | — | — | 5·1–8·3 | — | — | — |
| Pallite$^{117, 435}$ | $NaCa(Al,Fe)_6(OH,F)_9(PO_4)_4,3H_2O$ | — | — | — | — | — | — | — | — | — | — | — | — |
| Barbosalite$^{294, 315}$ | $Fe.OH.PO_4$ | 37·5 | — | — | — | — | — | 13·1 | 2·8 | 41·7 | — | — | 4·9 |
| Strunzite$^{323, 368}$ | $MnFe_2(OH)_2(PO_4)_2,8H_2O$ | 33·0 | — | — | — | — | — | — | 9·1 | 36·0 | — | — | 22·5 |
| Laueite$^{324}$ | $MnFe_2(OH)_2(PO_4)_2,8H_2O$ | 26·5 | — | — | — | — | — | — | 11·1 | 29·5 | — | — | 30·8 |
| Pseudo-laueite$^{331}$ | $MnFe_2(OH)_2(PO_4)_2,8H_2O$ | 27·0 | — | — | — | — | — | — | 11·1 | 28·0 | — | — | 31·0 |
| Cardosonite$^{350}$ | | 24·8 | — | — | — | — | — | — | — | 54·1 | — | — | 9·2 |
| Bassettite$^{322}$ | $Fe(UO_2)_2(PO_4)_2,8H_2O$ | 15·2 | — | — | — | — | — | — | — | 8·4 | 62·0 | — | 14·5 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | CuO | SrO | $Na_2O$ | $Al_2O_3$ | $CrO_3$ | MgO | PbO | $As_2O_5$ | $UO_3$ | F | $H_2O$ |
| Bergenite$^{275, 321}$ | $Ba(UO_2)_4(PO_4)_2(OH)_4,8H_2O$ | — | — | — | — | — | — | — | — | — | — | — | — |
| Boggildite$^{309–12}$ | $Na_2Sr_2Al_2.PO_4.F_9$ | 13·3 | — | 37·6 | 11·6 | 19·4 | — | — | — | — | — | 31·7 | — |
| Novacekite$^{292}$ | $Mg(UO_2)_2(AsO_4.PO_4)_2,nH_2O$ | 6·9 | — | — | — | — | — | 3·4 | — | 11·2 | 59·7 | — | 17·0 |
| Przhevalskite$^{340}$ | $PbO.(UO_2)_2.(PO_4)_2,4H_2O$ | 11·5 | — | — | — | 3·5 | — | — | 21·1 | — | 46·6 | — | 6·7 |
| Kingite$^{318}$ | $Al_2O_3.Al(OH)_3(PO_4)_2,9H_2O$ | 28·2 | — | — | — | 31·9 | — | — | — | — | — | 0·8 | 36·5 |
| Fornacite$^{413}$ | $(Pb,Cu,Fe)_3(AsO_4,PO_4,CrO_4)_2.OH$ | 0·7 | 10·9 | — | — | — | 11·8 | — | 57·2 | 15·0 | — | — | — |

### Table XVI.—(*continued*)

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | BaO | SrO | $Ce_2O_3$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $SiO_2$ | $ThO_2$ | F | $H_2O$ |
| Strontium apatite[354] | $Sr_6(Ca,BaMg)_3(PO_4.SiO_4)_6OH.F$ | 30·4 | 2·7 | 46·1 | — | 0·4 | — | 1·6 | 10·8 | 0·9 | — | 1·7 | 1·6 |
| Sigloite[355] | $FeAl_2(O.OH)_2(PO_4)_2,8H_2O$ | 27·5 | — | — | — | 21·1 | 16·5 | 0·9 | — | — | — | — | 33·6 |
| Lipscombite[343, 434] | $Fe_3(OH)_2(PO_4)_2$ | — | — | — | — | — | — | — | — | — | — | — | — |
| Smirnovskite[342] | $(Th,Ca,Ce,Al)(SiO_4.PO_4)(OH)_5F_4$ | 9·0–17·8 | — | — | 0·8–8·0 | 0·8–2·9 | — | — | 3·9–4·1 | 6·5–10·0 | 51·2–59·0 | 3·6–5·0 | 6·9–9·3 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | SrO | $Na_2O$ | $Ce_2O_3$ | $La_2O_3$ | $ThO_2$ | $UO_3$ | $SiO_2$ | $SO_3$ | $Fe_2O_3$ | $H_2O$ |
| Belovite[345, 412] | $(Na,Ca,Sr,Ce)_{10}(P,Si,SO_4)_6(OH)_2$ | 28·9–29·3 | 0·8–5·2 | 33·6–39·6 | 3·6–5·0 | 11·3–24·0 | 12·8 | — | — | 1·4 | 1·1 | — | 0·9 |
| Kivuite[336] | $ThH_2(UO_2)_4(OH)_8(PO_4)_2,7H_2O$ | 6·0 | — | — | — | — | — | 8·3 | 62·9 | — | — | — | 14·3 |
| Cheralite[344] | $(Ca,Ce,Th,La)(PO_4.SiO_4)$ | 26·8 | 6·3 | — | — | 14·2 | 13·4 | 31·5 | 4·1 | — | — | — | — |
| Ningyoite[313] | $CaU(\text{Rare earth})_2(PO_4)_2,2H_2O$ | 16·8–29·4 | 6·1–11·5 | — | — | — | — | — | 24·8–50·8 | — | — | — | 5·4–9·3 |
| Lermontovite[314] | $(CaU)_3(\text{Rare earth})_3(PO_4)_4,6H_2O$ | 20·4 | 1·0 | — | — | — | — | — | 53·5 | 2·4 | — | — | — |
| Grayite[337] | $Th_3(PO_4)_4$ | — | — | — | — | — | — | — | — | — | — | — | — |
| Sulphate monazite[356] | $(Ca,Th,\text{Rare earth})(P,S,Si)O_4$ | 25·8 | 4·6 | — | — | — | 50·6 | 5·8 | — | 1·1 | 3·1 | 6·1 | 3·5 |
| Pseudo autunite[418–19] | $Ca_{0\cdot86}(UO_2)_{1\cdot14}(PO_4)_2(H_3O)_2,2\cdot5H_2O$ | 23·0 | 7·8 | — | — | — | — | — | 53·1 | — | — | — | — |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $ThO_2$ | CaO | $Al_2O_3$ | $R_2O_3$* | $Fe_2O_3$ | $Bi_2O_3$ | $V_2O_4$ | $V_2O_5$ | $SiO_2$ | $SO_3$ | $H_2O$ |
| Schoderite[357] | $Al_4(VO_4.PO_4)_2,16H_2O$ | 17·4 | — | — | 23·8 | — | — | — | — | 24·6 | — | — | 34·1 |
| Metaschoderite[357] | $Al_4(VO_4.PO_4)_2,12H_2O$ | 19·1 | — | — | 26·0 | — | 0·3 | — | — | 27·0 | — | — | 27·9 |
| Gutsevichite[358] | $(Al,Fe)_3(PO_4.VO_4)_2(OH)_3,8H_2O$ | 16–17·6 | — | 2·7 | 24–26 | — | 2–4·7 | — | 2·3–2·9 | 11·7–14·1 | 1–3 | — | 30–33 |
| Waylandite[366] | $Al_3(Bi,Ca)(PO_4.SiO_4)_2(OH)_6$ | 22·2 | — | 2·90 | 29·3 | — | — | 28·3 | — | — | 4·7 | — | 12·9 |
| Saryarkite[414] | $(Ca,Al,Th,R)(SiO_4.SO_4.PO_4)_4OH,H_2O$ | 11·9–12·2 | 7·8–9·1 | 6·0–6·6 | 26·6–28·7 | 10·8–11·0 | 1·4–2·2 | — | — | — | 14·2–14·8 | 2·9–3·4 | — |
| Rusakovite[359] | $(Fe,Al)_5(VO_4.PO_4)_2(OH)_9,3H_2O$ | 6·5 | — | — | 5·0 | — | 45·0 | — | 5·0 | 16·6 | — | — | 18·3 |

* Rare earth oxides

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Al_2O_3$ | $Fe_2O_3$ | $Ce_2O_3$ | $La_2O_3$ | $ThO_2$ | $TiO_2$ | $SiO_2$ | $UO_3$ | $CO_2$ | $Nb_2O_5$ | $H_2O$ |
| Cerphosphorhuttonite[415] | $(Ce,Th)(PO_4.SiO_4),3H_2O$ | 10·0 | — | 3·4 | 11·9 | 12·8 | 40·6 | — | 10·0 | 1·6 | 1·6 | — | 6·4 |
| Karnasurtite[352] | $(La,Ce,Th,Ti,Nb,Al,Fe)(SiO_4.PO_4)_2(OH)_4,3H_2O$ | 2·4–6·8 | 5·5–8·4 | 0·8–3·5 | 5·2–17·6 | 8·6–10·6 | 2·8–6·2 | 6·7–12·3 | 20·5–30·3 | — | — | 2·8–8·2 | 10·7–17·9 |

*Table XVI.—(continued)*

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | $Al_2O_3$ | $Fe_2O_3$ | $Ce_2O_3$ | $La_2O_3$ | $ThO_2$ | $TiO_2$ | $SiO_2$ | CaO | $V_2O_5$ | $Nb_2O_5$ | $H_2O$ |
| Hydrocerite[378] | $(La,Ce,Th,Ca,Al,Fe,Ti,Nb)(SiO_4.PO_4)_2,5H_2O$ | 5·8 | 3·7 | 6·2 | 4·8 | 12·3 | 15·4 | 3·3 | 22·3 | 2·8 | — | 2·0 | 19·8 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | BaO | SrO | MnO | $Fe_2O_3$ | $TiO_2$ | $SiO_2$ | $SO_3$ | $Na_2O$ | $Ce_2O_3$ | FeO | $H_2O$ |
| Yoshimuraite[360] | $(BaSr)_2(TiFe)Mn_2(SiO_4)_2.SO_4.PO_4.OHCl$ | 4·0 | 33·5 | 4·6 | 17·6 | 1·8 | 10·0 | 18·3 | 5·4 | — | — | — | 2·3 |
| Manganoan lipscombite[365] | $(Fe,Mn)(Fe_2{}^{3+})(PO_4)_2(OH)_2$ | 33·4 | — | — | 7·9 | 50·5 | — | — | — | — | — | 3·7 | 4·5 |
| Schreibersite[362, 436] | $(FeNi)_3P$ | — | — | — | — | — | — | — | — | — | — | — | — |
| Lomonosovite[283, 284, 327–8] | $Na_2Ti_2Si_2O_9.Na_3PO_4$ | 8·2–12·8 | — | — | — | 2·4 | 24·4–25·3 | 24·1 | — | 23·8–28·1 | — | — | 0·3–2·2 |

| Name | Formula | Percentage composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $P_2O_5$ | BaO | SrO | $ThO_2$ | $Fe_2O_3$ | $Y_2O_3$ | CaO | $SiO_2$ | $CO_2$ | $Ce_2O_3$ | F | $H_2O$ |
| Brockite[389] | $(Ca,Sr,Ba,Ce,Th)(PO_4,CO_3),0{\cdot}9H_2O$ | 23·6 | 1·1 | 1·3 | 42·7 | 4·6 | — | 9·7 | — | 3·1 | 6·6 | — | 7·5 |
| Yttrian apatite[390] | $(Ca,Y)_5(PO_4)_3F.OH$ | 40·3 | — | — | — | 0·4 | 10·7 | 43·3 | 2·6 | — | — | 2·8 | 0·6 |

*Table XVII.—Index to Phosphorus Minerals*

| Name | % $P_2O_5$ | Page No. |
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| Davisonite | 30–33 | 47 |

*$P_2O_5$ content calculated from formula.

*Table XVII.—(continued)*

| Name | % $P_2O_5$ | Page No. |
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| Evansite | 18–22 | 50 |
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| Foucherite | 19–20 | 42, 47 |
| Francolite | 38–39 | 43, 47 |
| Frondelite | 32 | 51 |
| Globosite | 29 | 42 |
| Glucine | 36–39 | 53 |
| Gorceixite | 21–24 | 40, 48 |
| Gordonite | 33 | 48 |
| Goyazite | 15–31 | 40, 48 |
| Graftonite | 39–42 | 43, 47 |
| Grayite | 26* | 45, 54 |
| Griphite | 38–40 | 46 |
| Gutsevichite | 16–18 | 54 |
| Hagendorfite | 42 | 53 |
| Hannayite | 44–46 | 42, 49 |
| Harbortite | 34–36 | 42, 50 |
| Herderite | 43–45 | 47 |
| Heterosite | 38–44 | 43, 51 |
| Hibbenite | 29 | 43, 49 |
| Hinsdalite | 15 | 48 |
| Hopeite | 32 | 40, 43, 49 |
| Huhnerkobelite | 39–42 | 46 |
| Hurlbutite | 52–57 | 53 |
| Hureaulite | 38 | 40, 43, 51 |
| Hydrocerite | 6 | 45, 55 |
| Hydroxyapatite | 38–42 | 47 |
| Hydroxyherderite | 39–44 | 47 |
| Isoclasite | 30 | 47 |
| Isokite | 37 | 53 |
| Jezekite | 30 | 43, 46 |
| Jiningite | 6 | 45 |

*$P_2O_5$ content calculated from formula.

*Table XVII.—(continued)*

| Name | % $P_2O_5$ | Page No. |
|---|---|---|
| Kamiokalite | 18 | 52 |
| Karnasurtite | 2–7 | 45, 54 |
| Kehoeite | 27 | 43, 49 |
| Kingite | 28 | 53 |
| Kivuite | 6 | 54 |
| Kolbeckite | 34 | 43, 47 |
| Koninckite | 35 | 43, 50 |
| Kribergite | 31 | 43, 50 |
| Kryzhanovskite | 35 | 53 |
| Lacroixite | 29 | 43, 46 |
| Landesite | 32 | 51 |
| Laubmannite | 26 | 50 |
| Laueite | 26 | 44, 53 |
| Laxmannite | 0–9 | 41 |
| Lazulite | 44–46 | 41, 49 |
| Lehiite | 35 | 46 |
| Lermontovite | 20 | 54 |
| Lessingite | 1 | 40 |
| Leucophosphite | 27–35 | 40, 46 |
| Lewistonite | 32–38 | 46 |
| Libethenite | 26–30 | 49 |
| Likasite | 14 | 53 |
| Lipscombite | 33–4 | 54 |
| Liroconite | 3–4 | 40, 50 |
| Lithiophilite | 43–45 | 44, 46 |
| Lithiophosphatite | 60 | 52 |
| Lomonosovite | 8–13 | 40, 55 |
| Ludlamite | 30–34 | 51 |
| Lueneburgite | 30 | 50 |
| Lusungite | 23* | 52 |
| Magniotriplite | 30–34 | 53 |
| Mangan-alluaudite | 41–47 | 46 |
| Manganoan apatite | 39–41 | 53 |
| Manganoan lipscombite | 33 | 55 |
| Merrillite | 32 | 43, |
| Messelite | 37 | 40, 47 |
| Meta-schoderite | 19 | 54 |
| Meta-strengite | 37–39 | 50 |
| Meta-torbernite | 13–15 | 51 |
| Meta-variscite | 45 | 50 |
| Meta-vauxite | 28–30 | 50 |
| Meyersite | 29 | 43, 50 |
| Millisite | 34 | 43, 46 |
| Mimetite | 0–6 | 50 |
| Minyulite | 36 | 46 |
| Mitridatite | 17–31 | 41, 47 |
| Monazite | 24–30 | 45, 52 |
| Monetite | 52 | 47 |
| Montebrasite | 46–48 | 46 |
| Montgomeryite | 38 | 47 |
| Moraesite | 35 | 53 |
| Morinite | 33 | 41, 46 |
| Natromontebrasite | 44 | 46 |
| Natrophylite | 41 | 46 |
| Neomesselite | 37 | 53 |
| Newberyite | 41 | 42, 44, 48 |
| Ningyoite | 16–30 | 44, 54 |
| Novacekite | 7 | 53 |
| Overite | 38 | 47 |
| Palermoite | 42–47 | 44, 52 |

*$P_2O_5$ content calculated from formula.

*Table XVII.—(continued)*

| Name | % $P_2O_5$ | Page No. |
|---|---|---|
| Pallite | 26–28 | 53 |
| Parahopeite | 30–32 | 49 |
| Paravauxite | 27–30 | 50 |
| Parsonsite | 14–16 | 51 |
| Phosphoferrite | 35 | 51 |
| Phosphophyllite | 33 | 41, 49 |
| Phosphorrosslerite | 28 | 48 |
| Phosphuranylite | 9–12 | 41, 51 |
| Planerite | 34 | 43 |
| Plumbogummite | 17–23 | 50 |
| Pravdite | 3 | 45 |
| Przhevalskite | 11 | 53 |
| Pseudo-autunite | 23 | 45, 54 |
| Pseudo-laueite | 27 | 53 |
| Pseudo-malachite | 20–24 | 49 |
| Purpurite | 41–48 | 51 |
| Pyromorphite | 8–20 | 50 |
| Reddingite | 34–36 | 51 |
| Redondite | 40–43 | 43, 44, 50 |
| Renardite | 8–9 | 51 |
| Rhabdophane | 25 | 44, 45, 52 |
| Richellite | 25–29 | 43, 47 |
| Richmondite | 38 | 43, 49 |
| Rockbridgeite | 30–43 | 51 |
| Roscherite | 38 | 41, 47 |
| Rosieresite | 26 | 43 |
| Rusakovite | 6 | 54 |
| Sabugalite | 16 | 52 |
| Saléeite | 12–16 | 41, 51 |
| Salmonsite | 35 | 43, 51 |
| Sampleite | 32 | 49 |
| Sarcopside | 33–40 | 43, 48 |
| Saryarkite | 11–13 | 54 |
| Schertelite | 44 | 44, 49 |
| Schoderite | 17 | 54 |
| Scholzite | 36 | 53 |
| Schreibersite | 22–6 | 55 |
| Scorzalite | 43 | 41, 49 |
| Seamanite | 16 | 50 |
| Shen-t'u shih | 5 | 45 |
| Sicklerite | 43–45 | 46 |
| Sigloite | 28 | 54 |
| Silico-rhabdophane | 19 | 44 |
| Silico-smirnovskite | 3 | 44 |
| Sincosite | 31–32 | 52 |
| Smirnovskite | 9–18 | 45, 54 |
| Sodium autunite | 15 | 52 |
| Sodium uranospinite | 2 | 52 |
| Souzalite | 38 | 49 |
| Spencerite | 26 | 43, 49 |
| Spodiosite | 29–32 | 47 |
| Stercorite | 34 | 46 |
| Sterrettite | 40 | 50 |
| Stewartite | 39 | 44 |
| Strengite | 37–39 | 42, 50 |
| Strontium apatite | 30 | 45, 54 |
| Strunzite | 33 | 53 |
| Struvite | 28–29 | 42, 44, 49 |
| Sulphate monazite | 26 | 54 |
| Svabite | 0–13 | 48 |
| Svanbergite | 16–21 | 48 |
| Tagilite | 26–28 | 49 |

*Table XVII.—(continued)*

| Name | % $P_2O_5$ | Page No. |
|---|---|---|
| Tangaite | 42 | 44 |
| Taranakite | 35–39 | 41, 46 |
| Tarbuttite | 29 | 49 |
| Tavistockite | 30 | 42, 48 |
| Tavorite | 40 | 52 |
| Thorian britholite | 6 | 45 |
| Thorite | 6 | 45 |
| Thorogummite | 5 | 45 |
| Tinticite | 28–31 | 44, 50 |
| Titano-rhabdophane | 3–7 | 44, 45 |
| Torbernite | 13–15 | 51 |
| Triphylite | 41–46 | 44, 46 |
| Triplite | 31–33 | 48 |
| Triploidite | 30–33 | 51 |
| Trolleite | 46 | 44, 49 |
| Tsumebite | 10–12 | 50 |
| Tundrite | 3–7 | 45 |
| Turquoise | 30–35 | 49 |
| Uralolite | 38–39 | 53 |
| Uramplite | 16 | 52 |
| Uranocircite | 15 | 51 |
| Uranospathite | 4 | 52 |
| Variscite | 41–45 | 42, 43, 44 50 |
| Varulite | 42–45 | 46 |
| Vashegyite | 26–32 | 44, 50 |
| Vauquelinite | 0–9 | 41, 45, 52 |
| Vauxite | 30 | 50 |
| Vayrynenite | 40 | 53 |
| Veszelyite | 18–20 | 49 |
| Viseite | 20 | 41, 52 |
| Vivianite | 27–30 | 42, 43, 50 |
| Wagnerite | 40–43 | 44, 48 |
| Wardite | 35 | 41, 43, 46 |
| Wavellite | 32–35 | 42, 44, 50 |
| Waylandite | 22 | 54 |
| Weinschenkite | 28–31 | 40 |
| Wenzelite | 38–40 | 40, 51 |
| Whitlockite | 45–46 | 47 |
| Wilkeite | 14–32 | 47 |
| Wolfeite | 32–35 | 51 |
| Woodhouseite | 18 | 47 |
| Xanthoxenite | 38 | 47 |
| Xenotime | 25–36 | 52 |
| Yoshimuraite | 4 | 55 |
| Yttrian apatite | 40 | 55 |
| Zepharovichite | 35–38 | 44 |

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## SECTION II

# THE UTILIZATION OF PHOSPHORUS MINERALS

BY D. R. PECK

Numerous investigations have been made into methods of separating and extracting phosphorites which avoid the necessity of producing elemental phosphorus. The general aim has been to improve the quality of the phosphorite, or to convert it by relatively simple means into products of commercial value. The procedures used to achieve this involve physical, mechanical and chemical methods of separation.

## SEPARATION BY PHYSICAL AND MECHANICAL MEANS

The most general method of concentrating low-grade ores is some kind of flotation process. Under suitable conditions the $P_2O_5$ content of an ore may be increased from 10% to about 30% in this way.

In some of the earliest trials the phosphorite was pulped in the presence of shale oil fractions boiling at 170° to 250°C. and flotation carried out by adding 0·5 to 1·0% of a higher fatty acid. Neutral or slightly alkaline conditions favour the process, but impurities such as calcium carbonate, calcium fluoride and iron sulphide are also floated under these conditions.[1] A similar procedure using tar acids, sodium silicate (water glass) and petroleum sodium soaps (acidol) increases the $P_2O_5$ content of the phosphorite from 17% to about 30%.[2, 3] Carboxylic acids derived from the oxidation of paraffin or petroleum have been found to be more efficient flotation agents than oleic acid.[4] Naphthenic acid is useful as a gathering agent and pine oil as a froth producer.[5]

Physico-chemical investigations indicate that the nature of the surface of the mineral, as determined by its wettability, is the decisive factor in the efficiency of the flotation. Wettability isotherms of phosphorites are a useful means of determining their floatability and of evaluating the activity of flotation agents.[6]

Grain size should be adjusted to the type of phosphorite used, otherwise low yields are obtained due to excess mud carrying off large proportions of phosphorite.[7]

Studies of the effect of various gases on the flotation of phosphate ores, using sodium carbonate, sodium silicate and tallow soap as flotation agents, show that a nitrogen atmosphere decreases the $P_2O_5$ recovery and that oxygen gives a noticeable increase. This effect is thought to be due to the sorption of oxygen molecules which increase the hydrophobicity of the mineral surface, with a corresponding increase in the thickness of the sorption layer of the collector.[8] Measurement of the angle of contact between the mineral surface and the flotation medium confirmed that air and oxygen increase the hydrophobic nature of the phosphorite. Graphs have been given which show the relationship between the size of the contact angle and the length of the period of contact of the mineral surface with the collector.[9] Other data show the effect on the $P_2O_5$ recovery of particle size of the ore and the duration of the treatment of the pulp with the gas. The action of the gases did not appear to be related to any chemical action on the collector.[10]

The efficiency of flotation may be increased by preliminary roasting of the phosphorite. This removes organic matter and water of crystallization, causes partial dissociation of calcium carbonate and also results in some removal of fluorine.[11] With some ores this treatment increases the flotation speed by 50 to 100% and reduces the amount of flotation agent required to about one-third.[12, 13] A preliminary mild treatment of a phosphorite with acid also leaves a residue which may be more readily upgraded by flotation.[287]

Preliminary grinding of the phosphorite improves the $P_2O_5$ recovery, the best results being obtained with particles 0·15 mm. (approximately 150 mesh) in size.[14]

Some phosphorites contain gypsum and similar impurities which tend to be transferred from the ore into the phosphorite solution during flotation. In such instances a pre-flotation washing of the ore with sodium chloride solution shortens the flotation time and decreases the amount of carboxylic acid needed.[15]

Numerous flotation procedures have been worked out for enriching phosphorites on a commercial scale. These vary with the type of ore used and with its $P_2O_5$ content.[16–21]

Mechanical procedures for separating phosphate ores depend largely on the type of phosphorite and the nature of the impurities associated with it. For example, simple washing with water and screening may be sufficient to increase the $P_2O_5$ content from 16 to 18%.[22] Usually, however, more complicated procedures are necessary if ores containing about 10% $P_2O_5$ are to yield concentrates with a $P_2O_5$ content of 20 to 25%.[23] Iron-containing ores, for example, are improved by ignition and grinding followed by magnetic separation to remove the magnetite formed,[24] and air-separation to remove the gangue.[25]

A picking process has been devised for particles greater in size than 1·0 mm., which are not easily separated by flotation. The phosphorite is first treated with a 1% aqueous solution of sodium palmitate containing up to 2% of oil or petroleum. It is then brought into contact with a surface coated with a hydrophobic organic substance such as bitumen. After about two minutes the phosphorite grains adhere to the surface, whereas others, such as quartz, do not. If ice is used as the surface, the process is reversed and only the quartz grains are picked up. A 90 to 98% separation has been achieved in this process, using phosphorite particles 5 to 30 mm. in size.[26]

A combination of mechanical and flotation processes is most generally used in America. Florida pebble phosphate is screened to separate the $\frac{1}{16}$ to 1 in. pebbles, using water sprays and vibrating screens. The smaller particles are further separated to give a fraction which is retained on a 48-mesh screen and a second fraction which passes the latter but stays on a 150-mesh screen. The second fraction is then floated at pH 8·5, using sodium hydroxide, tall oil and fuel oil as flotation agents. The recovery is 92% and the product contains 5·5% silica. The latter is reduced to 3% and the $P_2O_5$ content increased to 36% by a second flotation stage using pine oil, sodium hydroxide and a cationic agent (usually an amine). The Tennessee deposits, which are generally of higher grade and contain 23 to 35% $P_2O_5$, are mostly separated mechanically by means of screens, hydro-separators, scrubbers, rakes and similar equipment.[27]

## SEPARATION BY CHEMICAL MEANS

Chemical treatment of phosphorites has been examined not only for extraction of the phosphorus but also for simultaneous production of other materials of commercial value.[29] The more common processes involve some form of acid treatment.[28] The type of treatment and the conditions under which the ore reacts are largely influenced by the variety and composition of the phosphorite, and by the nature of the desired end-product. The latter may not be a pure material and if the complete separation of a pure product, e.g. phosphoric acid, is required, further purification stages may be necessary.

### Decomposition with Hydrochloric Acid

Phosphorites are fairly easily decomposed by treating the ore, ground to 20-mesh size, with the theoretical amount of 10% aqueous hydrochloric acid. After filtration of the reaction mixture, the phosphoric acid may be precipitated as calcium phosphate by addition of ground limestone and allowing sufficient time for neutralization. In practice, however, it is an advantage to complete the reaction by using milk of lime.

The action of very dilute hydrochloric acid varies with the origin of the phosphorite, some ores being more easily decomposed than others. With 1% hydrochloric acid a 70 to 90% reaction is usually obtained at 18°C. This increases to 80 to 92% with 5% acid. In both instances the amount of acid used is sufficient to convert all the calcium in the ore into calcium chloride. For acid concentrations of 3% or less, part of the hydrochloric acid can be replaced by sulphuric acid.[30]

Pure phosphoric acid is claimed to result from the extraction of phosphate rock–hydrochloric acid mixtures with organic solvents such as ketones, butanol, pentanol or *iso*amyl alcohol which have a limited solubility in water.[31, 288–9] From the aqueous layer phosphoric acid of about 75% concentration is obtained. It is substantially free from metallic impurities except for calcium. The organic solvent is recovered by distillation.

When very low grade glauconitic ore is extracted with hydrochloric acid for 1 hr. at 80°C., the amount of iron removed is minimized by calcining the ore for 2 hr. at 1050°C. Increasing the time to 4 hr. doubles the amount of silica extracted.[32]

The distribution coefficient $K_d = c\,\underset{\text{aq.}}{\mathrm{H_3PO_4}} \Big/ c\,\underset{\text{org.}}{\mathrm{H_3PO_4}}$ for phosphoric acid between water and a series of straight-chain alcohols is found to obey the empirical relationship $K_d = 1/(an_c - b)$, where $a$ and $b$ are constants, and $n_c$ is the number of atoms in the $C_4 - C_{10}$ chain. The extractibility of the common mineral acids increases in the order $HNO_3 < HCl < H_2SO_4 < H_3PO_4$. 87·2% of the total phosphoric acid can be extracted by *n*-butanol from a native phosphorite treated with nitric acid.[290] Tributyl phosphate is also an excellent solvent for phosphoric acid.[291] Even more efficient purification is achieved by the use of solvents which:

(*a*) extract practically no phosphoric acid from aqueous solutions containing less than 35% $H_3PO_4$,
(*b*) extract significant amounts of acid at concentrations above 35% $H_3PO_4$, the amount increasing with increasing concentration,
(*c*) dissolve more phosphoric acid at low rather than at high temperatures.

Dibutyl ether is a particularly good solvent of this kind, and by using it to extract 86·5% phosphoric acid at low temperature, warming the extract and adding a small amount of water, an aqueous phosphoric acid is obtained of similar concentration to the original, but containing only a small proportion of the bases originally present.[292] An extensive review of earlier literature on the extraction of phosphoric acid has appeared.[288]

In some procedures the hydrochloric acid is generated *in situ* by using sulphuric acid and sodium, potassium, ammonium or magnesium chlorides. The amount of calcium extracted by this method varies with the salt used. If required for use as a fertilizer, the best product is said to result from treatment of the phosphorite with a mixture containing 2·5% $H_2SO_4$, 0·9% NaCl and 0·5% $MgCl_2$.[33] The rate of decomposition decreases when ammonium chloride is used in conjunction with hydrochloric and sulphuric acids.[34]

Hydrochloric acid and ammonium sulphate have been used to extract phosphate rock for fertilizer purposes. Calcium chloride and a mixture of mono- and dicalcium phosphates are obtained by an initial acid extraction. The product is then caused to react with ammonium sulphate to give a material containing 15% $P_2O_5$ and 7·4% nitrogen.[35]

A more unusual procedure involving treatment of phosphate rock with concentrated hydrochloric acid, ferric chloride, milk of lime, coke dust and chlorine has been described. Phosphorus oxychloride is distilled out as an intermediate product and is then hydrolyzed to phosphoric and hydrochloric acids. The latter is re-used.[36]

Phosphorites have been extracted by reaction with gaseous hydrogen chloride at 500° to 600°C.[37] Unground phosphate ores react very rapidly at 120° to 300°C. with gaseous nitric acid or hydrogen chloride to give a highly concentrated hot magma.

The latter is only slightly acid because of the low solubility of the gaseous reactants in the melt at the temperatures used. The product is non-hygroscopic and contains 15% $P_2O_5$ and 12% N. The process is suitable for continuous operation in towers.[38–9]

### Decomposition with Nitric Acid

The use of nitric acid may offer economic advantages over other acid processes when the product is used as a fertilizer. For example, the nitrogen value of the product can compensate for the higher cost of nitric acid as compared with that of sulphuric acid.[40, 293, 294] Numerous variations in processes involving nitric acid have been reported, of which the following are typical.

In one process a phosphorite containing 22% $P_2O_5$ and 39% CaO is ground to 150 to 200-mesh size and is then stirred for 1 to $1\frac{1}{2}$ hr. at room temperature with a 5% excess of 15 to 40% nitric acid. Maximum extraction (95%) of the $P_2O_5$ occurs when acid of 25% concentration is used. The extraction decreases to 60% if only 95% of the stoicheiometric amount of acid is added.[41] At 50°C. the maximum decomposition of phosphorite occurs with 14 to 25% nitric acid. Higher acid concentrations, increase in temperature and addition of sodium sulphate all tend to decrease the rate of decomposition.[42] Increasing both the temperature and the acid concentration increases the amount of base metals extracted from the ore.[43] Removal of fluorine is said to result from treating phosphorite with 43% nitric acid at 60°C. and then adding sericite (a sodium aluminium silicate mineral) and filtering.[44]

In order to obtain a less hygroscopic product, phosphorite is sometimes treated for 30 min. with only enough 25% nitric acid to decompose the calcium carbonate and tricalcium phosphate in the ore. Enough ammonia and ammonium carbonate are then added to precipitate the phosphorus and calcium as dicalcium phosphate and calcium carbonate.[45] Ammonium nitrate is obtained by evaporating the filtrate, but the product is hygroscopic owing to the presence of calcium nitrate. The latter is eliminated by carrying out the process in two stages and filtering off the calcium carbonate at 45° to 50°C.[46]

When ammonia is used in conjunction with nitric acid it is important to control the pH during the neutralization stage, otherwise complete recovery of the phosphorus does not take place. The optimum conditions for conversion into dicalcium phosphate of the monocalcium salt formed in the initial reaction of the phosphorite with nitric acid are a temperature of 60°C. and $P_2O_5$ and $N_2O_5$ concentrations in solution of not more than 6 and 21%, respectively.[47] Filtration of the precipitated calcium carbonate is improved if the ammonium carbonate is added at 40° to 45°C., using a 10 to 15% excess of a 25 to 30% solution. If the reaction is carried out with gaseous ammonia and carbon dioxide instead of ammonium carbonate, the rate of precipitation depends on the rate at which ammonium carbamate is hydrolyzed in solution.[48]

Phase diagrams relevant to the action of nitric acid on phosphorites have been studied by a number of authors. Diagrams for the $Ca(NO_3)_2$–$HNO_3$–$H_3PO_4$–$Ca_3(PO_4)_2$–$H_2O$ system at 5°, 25°, 50°, 75° and 100°C.[49] and for the solubility of calcium nitrate in the $Ca(NO_3)_2$–$H_3PO_4$–$HNO_3$–$H_2O$ system[50] have been given. Metastable equilibria in the $CaO$–$P_2O_5$–$H_2O$[51] and $Ca(NO_3)_2$–$HNO_3$–$H_2O$[52] systems have been studied. The influence of ammonium ions on these systems has been investigated in detail.[53–8] Some of the data[59–63] enable yields of mono- and dicalcium phosphate, obtainable by dissolving phosphorite in nitric acid of known concentration, to be calculated. The effect of adding ammonia to the system can also be determined.[64–6]

Phosphate ores of the fluorapatite type are less readily decomposed by nitric acid than are phosphorites. At 50°C. using 120% of the nitric acid required for the reaction:

$$3Ca_3(PO_4)_2{,}CaF_2 + 14HNO_3 = 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF$$

the decomposition is rapid during the first ten minutes, but decreases quickly as the CaO and $P_2O_5$ concentrations increase in the solution. At a later stage the soluble

$P_2O_5$ concentration decreases because monocalcium phosphate precipitates on the undecomposed fluorapatite and so reduces the decomposition rate. A diagram has been given which shows the optimum conditions for obtaining maximum yields of monocalcium phosphate and calcium nitrate in a cyclic process.[67] After filtering off the phosphate, the calcium nitrate is removed by crystallizing at 5°C. or at $-30$°C. At the latter temperature the equilibrium concentrations in solution are 29 to 39% $P_2O_5$, 2·3 to 3·9% CaO and 40 to 53% $H_3PO_4$.[68] A saving of 20 to 30% of the nitric acid used is said to occur when fluorapatite is treated at 60° to 100°C. with a 40 to 50% nitric acid solution containing 40% ammonium sulphate.[69] Iron and magnesium are reported to inhibit the conversion of the extracted phosphate into a citrate-insoluble form during the neutralization of nitric acid extracts of apatite with ammonia.[70]

Alternatively, after crystallization of calcium nitrate at low temperature, the residual nitric acid is removed as barium nitrate by the addition of barium carbonate. The residual phosphoric acid, after precipitation of calcium by sulphuric acid, is comparable in quality with gypsum process acid, while the nitric acid is recovered as ammonium nitrate for fertilizer use by treatment with carbon dioxide and ammonia.[294]

In most types of phosphate rock the $CaO:P_2O_5$ ratio is greater than that for dicalcium phosphate, so that invariably a product containing calcium nitrate is obtained when the ore reacts with nitric acid. The addition of ammonia in this process is assumed to give a mixture of dicalcium phosphate, calcium fluoride, calcium nitrate and ammonium nitrate, and the phosphates of any iron and aluminium present in the rock. For practical purposes the requirement of ammonia is calculated from the expression:

$$NH_3 = NO_3 + 0{\cdot}395P_2O_5 + 0{\cdot}737F - 0{\cdot}5CaO - 0{\cdot}55Al_2O_3 - 0{\cdot}35Fe_2O_3$$

where the symbols represent the weight in grams of each component in the system. The reaction mixture is often adjusted with sulphuric or phosphoric acid so as to avoid the presence of soluble calcium salts on subsequent neutralization with ammonia. The filtered solution then contains monoammonium phosphate instead of calcium nitrate, and for this the ammonia requirement is given by:

$$NH_3 = NO_3 + 0{\cdot}197P_2O_5 + 0{\cdot}368F - 0{\cdot}25CaO - 0{\cdot}275Al_2O_3 - 0{\cdot}175Fe_2O_3$$

The precipitation of dicalcium phosphate is assumed to take place according to the equation:

$$3Ca(H_2PO_4)_2 + 3Ca(NO_3)_2 + 6NH_3 = 6CaHPO_4 + 6NH_4NO_3$$

Under some conditions, however, the reaction is:

$$\begin{aligned}&3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 14NH_3 + 2H_2O\\&\qquad = 3Ca_3(PO_4)_2,Ca(OH)_2 + 14NH_4NO_3\end{aligned}$$

so that more than the calculated amount of ammonia is required.

Complete extraction of the rock occurs when the acid ratio (moles $N_2O_5$ to moles CaO) is 0·90 to 0·95. Fluorine in the ore, however, promotes the precipitation of an apatite. This can be avoided by removing most of the fluorine at the ammoniation stage. Neutralization of the acid extract at 30° to 40°C. with 40 to 50% of the required amount of ammonia, so as to bring the pH to 0·9 to 1·4, removes over 90% of the fluorine as calcium fluoride. The iron and aluminium are also removed as secondary phosphates, $R_2(HPO_4)_3$. Approximately 15% of the phosphorus in the extract is precipitated in this operation. After removal of the initial precipitate the phosphorus is recovered from the filtrate by addition of more ammonia so as to bring the total amount used to 110% of the calculated amount.[71]

Ammonia is used in processes based on the nitric acid extraction of phosphate ores so as to avoid the presence of calcium nitrate in the end product. In one procedure phosphate rock reacts with 53% nitric acid and the solution is partly neutralized with ammonia to form dicalcium phosphate which is filtered off. The filtrate is then treated with ammonia and carbon dioxide until the pH is 6 to 8. The main product is a carbonate apatite approximating to $Ca_{10}(PO_4)_6CO_3$ in composition.[72] A similar process uses ammonia and sulphur dioxide in the final stage. This gives a citrate-soluble material containing ammonium nitrate and a phosphate in which the molar ratio of CaO, $P_2O_5$ and $SO_2$ is 3·7:1:0·7.[73]

### USE OF SULPHURIC ACID AND NITRIC ACID

Sulphates and sulphuric acid have been used in conjunction with nitric acid and ammonia to produce materials which are both non-hygroscopic and non-caking. The composition of the products is often not known precisely, but it appears that calcium nitrate is eliminated and is replaced by calcium sulphate, calcium carbonate or dicalcium phosphate, together with an equivalent amount of ammonium nitrate. For example, Florida phosphate rock reacts with 42% nitric acid in proportions to give a molar $HNO_3/CaO$ ratio of 1·8. Ammonia is then added at 80°C. to give a molar $NH_3/NO_3$ ratio of 0·63, sufficient potassium sulphate also being present to give a $K_2O/P_2O_5$ weight ratio of unity. Ammonium sulphate can be used instead of the potassium salt and potash minerals, such as langbeinite ($K_2O$ 21·4, MgO 19·0, $SO_4$ 67%) and glaserite ($K_2O$ 41·6, $Na_2O$ 7·1, $SO_4$ 56·5%), are an alternative source of sulphate. The quantities of these minerals used are such as to give a $K_2O/P_2O_5$ weight ratio of 0·29 with langbeinite and 0·67 with glaserite. The products have a high citrate-solubility under the above conditions, but the $P_2O_5$ availability decreases sharply if the $HNO_3/CaO$ ratio is less than 1·8 or if the sulphate is added after the ammonia stage.[74] In a modification of this procedure, much smaller quantities of sulphate are used and the final stage is carried out with an equimolar mixture of carbon dioxide and gaseous ammonia until the $NH_3/NO_3$ molar ratio is 0·95. The product contains dicalcium phosphate, calcium carbonate and ammonium nitrate.[75]

With mixtures of nitric and sulphuric acids the efficiency of extraction of apatite is only slightly affected by the addition of up to 10% nitric acid. However, when the content of the nitric acid in the mixture is between 40 and 90%, over 96% of the phosphate is extracted in 15 min. at 50°C.[76]

A non-caking product is formed when Moroccan phosphate reacts with a mixture containing equal equivalents of nitric and sulphuric acids. The total acid concentration in this procedure is 66% and the amount used is 80% based on the CaO content of the rock. The reaction is vigorous and the product contains 23% of calcium nitrate, together with 90% of the fluorine originally present in the ore. If potassium chloride is added, the product becomes hygroscopic. In both cases the reaction mixture is adjusted to pH 6 with ammonia.[77]

In a similar procedure, ground Florida phosphate is caused to react at 70°C. with a mixture containing 15% $H_2SO_4$, 29% $HNO_3$ and 56% $H_2O$ in proportions corresponding to the equation:

$$Ca_{10}F_2(PO_4)_6 + 12HNO_3 + 4H_2SO_4 = 6H_3PO_4 + 6Ca(NO_3)_2 + 4CaSO_4 + 2HF$$

The mixture is then adjusted to pH 3·7 with gaseous ammonia to bring about the reaction:

$$\begin{aligned} &6H_3PO_4 + 6Ca(NO_3)_2 + 4CaSO_4 + 2HF \\ &\qquad = 12NH_4NO_3 + 5CaHPO_4 + NH_4H_2PO_4 + 4CaSO_4 + CaF_2 \end{aligned}$$

Under these conditions 98% of the phosphorus in the product is citrate-soluble.[78]

### USE OF PHOSPHORIC ACID AND NITRIC ACID

Phosphoric acid is frequently used, together with nitric acid and ammonia, for treating phosphorites, particularly where the product is used as a fertilizer. Many processes of this kind have been devised, of which the following is typical.

Florida rock of 30-mesh size is treated at 40° to 50°C. with a mixture of 42% nitric acid and 80% phosphoric acid in the proportions required by the equation:

$$Ca_{10}F_2(PO_4)_6 + 20HNO_3 + 4H_3PO_4 = 10Ca(NO_3)_2 + 10H_3PO_4 + 2HF$$

The amount of phosphoric acid used is such that the total $P_2O_5$ (i.e. the sum of the $P_2O_5$ in the rock and that in the added phosphoric acid) in the system is one mole for every two moles of CaO. Complete extraction occurs when the molar ratio $(HNO_3+H_3PO_4)/CaO$ is 2·1 or more. About 30% of the fluorine in the rock is volatilized at this stage.

The reaction mixture is now treated with gaseous ammonia at 90° to 110°C. in an amount required by the equation:

$$10Ca(NO_3)_2+10H_3PO_4+2HF+21NH_3 = 20NH_4NO_3+9CaHPO_4+NH_4H_2PO_4+CaF_2$$

The final pH is 3·7 to 4·0, the product is relatively non-hygroscopic and 98% of the phosphorus in it is available to plants.

The neutralization with ammonia in this process is carried out in four stages in which 57, 26, 13 and 4% of the total requirement is used. Single stage treatment, or neutralization to a higher pH than 4, considerably decreases the amount of available phosphorus in the product. This is due to the formation of fluorapatite, probably by a reaction such as the following[79]:

$$10Ca(NO_3)_2+10H_3PO_4+22{\cdot}8NH_3+1{\cdot}4HF = 0{\cdot}7Ca_{10}F_2(PO_4)_6+3CaHPO_4+2{\cdot}8NH_4H_2PO_4+20NH_4NO_3$$

This phenomenon has been observed in other extraction procedures.[71, 74–5]

In processes involving neutralization with ammonia, reversion of the phosphate to a citrate-insoluble or non-available form is a frequent occurrence. This happens when the ammonia addition is not controlled, or neutralization is carried to too high a pH value. There are conflicting reports as to how this may be avoided. Addition of salts of magnesium, aluminium, zinc, molybdenum, vanadium, manganese, iron, chromium, nickel and cobalt is said to enable the neutralization to be made up to pH 9.[80] The most effective salts appear to be magnesium, aluminium and manganese sulphates.[81] The sulphate ion alone seems to be equally effective because a similar action has been observed with sulphuric acid and alkali sulphates.[74–5] On the other hand the effect of these additions has been stated to be negligible and removal of 90% of the fluorine by controlled ammoniation is recommended.[71] It has also been proposed to remove the fluorine by adding silica to the acid extract, adjusting the $CaO:P_2O_5$ molar ratio to less than 2 and removing calcium nitrate by crystallization. Ammonium and sodium nitrates are then added and this precipitates 80% of the fluorine as sodium silicofluoride.[82]

### Decomposition with Sulphuric Acid

Sulphuric acid is the acid most generally used for extracting phosphorites. The methods and techniques adopted depend on whether the product is a fertilizer or wet-process phosphoric acid. For the latter it is important to have a pure material and the removal of trace impurities of fluorine, silica, iron and heavy metals is not easy to achieve.

Many investigations into the production of wet-process phosphoric acid have been made and this work has been well summarized and reviewed.[83] The following is a brief description of the procedure used when fluorapatite is the raw material.

The simplest representation of the reaction is given by the equation:

$$Ca_{10}F_2(PO_4)_6+10H_2SO_4+20H_2O = 10(CaSO_4,2H_2O)+6H_3PO_4+2HF$$

However, since phosphate rock is not pure calcium fluorapatite but contains impurities such as silica, iron, aluminium and carbonate, closer approximation to the reactions involved is given by the following series of equations:

$$(1)\quad Ca_3(PO_4)_2+3H_2SO_4+6H_2O = 3(CaSO_4,2H_2O)+2H_3PO_4$$
$$(2)\quad CaF_2+H_2SO_4+2H_2O = CaSO_4,2H_2O+2HF$$
$$(3)\quad 4HF+SiO_2 = SiF_4+2H_2O$$

$$2SiF_4+2H_2O = H_2SiF_6+SiO_2+2HF \tag{4}$$
$$6HF+SiO_2 = H_2SiF_6+2H_2O \tag{5}$$
$$H_2SiF_6 \rightleftharpoons SiF_4+2HF \tag{6}$$
$$CaF_2+H_3PO_4 = Ca(H_2PO_4)_2+2HF \tag{7}$$
$$H_2O+CaCO_3+H_2SO_4 = CaSO_4{,}2H_2O+CO_2 \tag{8}$$
$$Fe_2O_3+2H_3PO_4 = 2Fe^{3+}+2PO_4^{3-}+3H_2O \tag{9}$$
$$Al_2O_3+2H_3PO_4 = 2Al^{3+}+2PO_4^{3-}+3H_2O \tag{10}$$

In practice some weak re-cycled phosphoric acid is used to produce the initial slurry of phosphate rock.[84, 295–6] The following reaction then occurs:

$$Ca_3(PO_4)_2+4H_3PO_4+3H_2O = 3[Ca(H_2PO_4)_2{,}H_2O] \tag{11}$$

The monocalcium phosphate is later decomposed by sulphuric acid:

$$3[Ca(H_2PO_4)_2{,}H_2O]+3H_2SO_4+3H_2O = 6H_3PO_4+3(CaSO_4{,}2H_2O) \tag{12}$$

The last two equations represent the initial reaction of the phosphate rock more closely than does equation (1). This reaction involves dissolution of the rock according to (11) and the subsequent crystallization of gypsum. It is important to ensure that the rate of solution of the apatite does not exceed the rate of transfer of calcium ions from the rock to the gypsum surface. Excessive concentration of rock or of sulphate ion causes supersaturation near the rock surface and the formation of fine calcium sulphate crystals which may coat the rock particles and retard the reaction.[85]

Reactions (2) to (7) are not quantitative. Varying amounts of fluorine are found in the solid, liquid and gaseous phases of the reaction. The quantity volatilized as silicon tetrafluoride depends on the reaction conditions, but is largely influenced by the concentration of the sulphuric acid used and by the proportion of acid to phosphate. Various estimates state[83, 86–8] that 15 to 40% of the fluorine is removed by volatilization, 10 to 30% in the gypsum and that 50 to 60% remains in the filtered phosphoric acid. On concentrating this acid to 30–50% $P_2O_5$ further volatilization occurs, to give phosphoric acid containing about 30% of the fluorine which was originally present in the phosphate rock.

Carbonate in the ore is a disadvantage in that it consumes sulphuric acid to no purpose (reaction 8). It also causes practical difficulties with foaming of the reaction mixture.

Iron and aluminium are also objectionable in wasting sulphuric acid (reactions 9 and 10) and in decreasing the amount of phosphoric acid available, e.g. in the manufacture of superphosphate.[89]

Practical details of the wet-acid process are given in many references[77, 84, 86, 87, 90–6] and only the main features are referred to here. Other details are to be found below in the description of the reaction of phosphorites with sulphuric and phosphoric acids (see pages 81 to 90).

The efficiency of the wet-acid process is very dependent on the careful preparation of the correct size and shape of gypsum crystals.[97] Of the three forms of calcium sulphate—dihydrate, hemihydrate and anhydrite—only the last is stable in the range of acid concentration normally found in wet-acid procedures. Extensive studies have been made of the transitions of the crystal hydrates of calcium sulphate in the presence of phosphoric acid[98–9, 106] and on the $CaO–P_2O_5–H_2O$[100] and $CaO–P_2O_5–SO_3–H_2O$[101] systems. The effects of temperature and acid concentration on the degree of hydration of calcium sulphate are shown in Fig. 1. The data used in constructing this diagram are derived from the thermodynamic properties of gypsum,[102] investigations of the $CaSO_4–H_3PO_4–H_2O$ system[103, 99] and observations on wet-process phosphoric acid manufacture.[96] During the initial stages of the reaction of phosphate rock with sulphuric acid the system is in the region above the line AB.[104] In the region below this the rate of transformation of hemihydrate into anhydrite and dihydrate is delayed,[105] probably as the result of supersaturation.

The rate of transformation and the size and shape of the calcium sulphate crystals are affected by the metallic and organic impurities in the rock,[104] by the addition of surface active materials such as arylsulphonic acids,[297] and by the concentration of unreacted sulphuric acid. In supersaturated solutions nucleation occurs only above a threshold value and under practical conditions the rate of crystal growth is proportional to the supersaturation. The theory of this has been discussed.[105]

The ratio of acid to rock has a marked influence on the filterability of the reaction mixture and deviations from the optimum ratio considerably reduce the filtration rate. Similar effects are found with too high phosphoric acid concentrations. Control of the solids concentration in the system is also necessary, but this is rather less critical than are factors involving the acids.

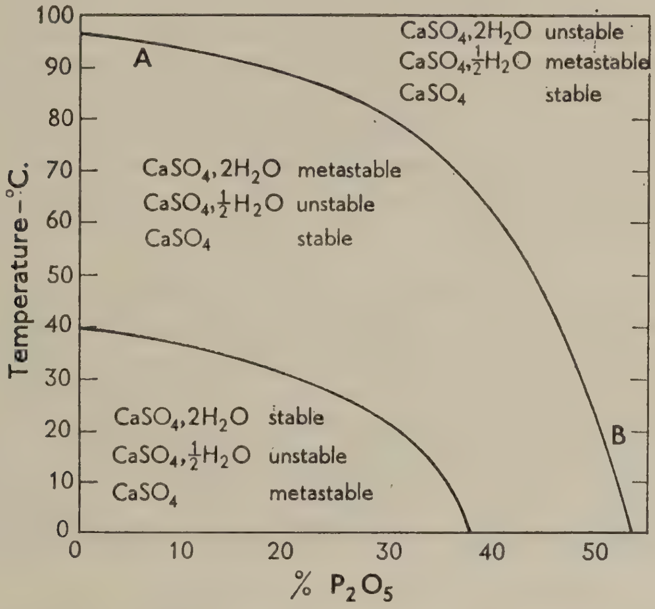

FIG. 1.—Effect of temperature and acid concentration on the form of calcium sulphate precipitated in the decomposition of phosphate rock

The kinetics of the reaction of sulphuric acid with phosphate rock have been extensively studied. Many of the data refer to the conditions used in production of superphosphate fertilizers rather than of wet-process acid. The following information is typical of that available in the literature.

### DECOMPOSITION OF PHOSPHATE ROCK

From a study of the reaction of Moroccan phosphate with 45 to 76% sulphuric acid at 80° to 105°C. it is concluded that for all acid/rock ratios the maximum conversion occurs with 70% sulphuric acid. In the initial stages, when free sulphuric acid is present, the main reaction is to form free phosphoric acid. This stops when the free sulphuric acid has disappeared and the reaction is then between phosphoric acid and unreacted phosphate to form monocalcium phosphate. After three weeks a stationary state is reached in which substantial proportions of free acid and unreacted phosphate remain. This is largely due to coating of the latter with calcium sulphate.[107] The effect of particle size of the ore on the time required for the free sulphuric acid to disappear from the reaction mixture is shown in Fig. 2.

Similar results were found with Florida pebble phosphate, the maximum conversion occurring with 60% to 70% sulphuric acid. The optimum acid concentration varied slightly with the time and temperature of the reaction. Addition of nitric acid or of sodium or ammonium nitrate increased the extraction rate, irrespective of variations in other factors. The acidulation ratio, i.e. the mole ratio of acid used to CaO in the ore, had an optimum value of 1·10 to 1·15. The optimum reaction temperature range, which depended on other reaction conditions, was 35° to 80°C. Empirical equations were derived which correlated the $P_2O_5$ extracted with acid concentration, reaction time and temperature, acidulation ratio, and the particle size of the rock.[108]

A linear relationship in which the percentage conversion of Florida phosphate varies from 90%, when using 76·5% sulphuric acid, to 98% with 52·5% acid has been found.[109] The only significant difference from the other observations[107–8] appears to be the higher reaction temperature of 120° to 130°C. The effect of acid ratio at this temperature when using 60% sulphuric acid is shown in Fig. 3.[109] The best practical sulphuric acid concentration is said to be 62%.[110]

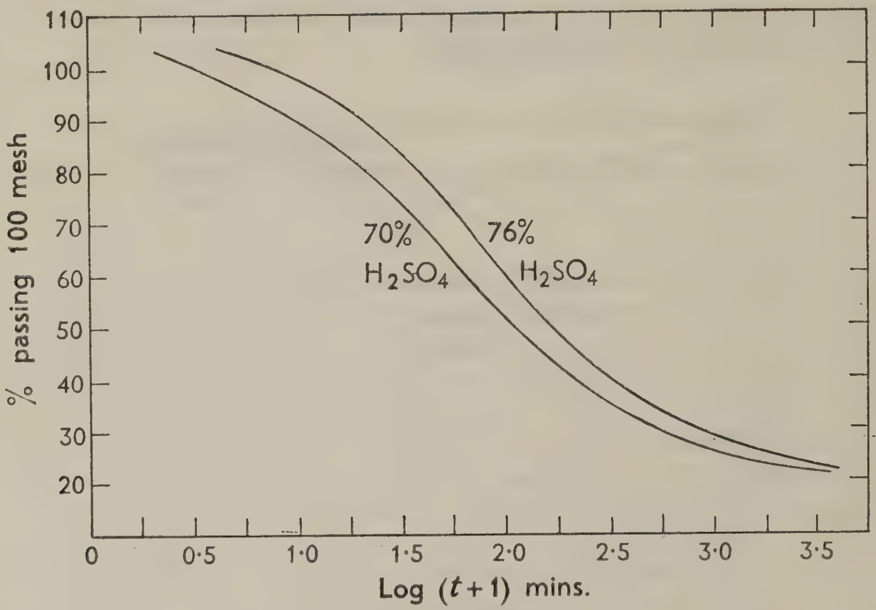

FIG. 2.—Rate of reaction of Moroccan phosphate with sulphuric acid

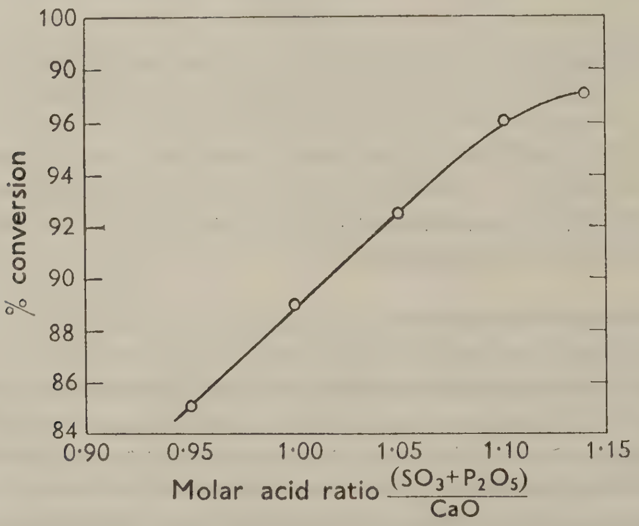

FIG. 3.—Effect of acid ratio on the reaction of Florida phosphate with sulphuric acid

During the mixing of sulphuric acid with apatite the amount of decomposition $K$ varies with the acid concentration and the weight ratio $R$ of acid to apatite according to the expression:

$$K = \frac{60R}{(1+0{\cdot}6A)\times 1{\cdot}38B}$$

where $A$ is percentage of phosphoric acid formed in the reaction mixture and $B$ is the percentage of $P_2O_5$ in the apatite. $K$ is maximal in 58% sulphuric acid when $R$ is 0·7.[111]

Too high a concentration of sulphuric acid inhibits the reaction with apatite and for a given temperature there is a concentration at which the reaction stops. As the temperature is raised so the concentration at which this occurs decreases.[112]

Several modifications of the wet-acid processes described above have been proposed, largely with the aim of making more concentrated phosphoric acid. In one of these the reaction temperature and sulphuric acid concentration are increased so as to precipitate calcium sulphate as the hemihydrate. This produces phosphoric acid containing 40 to 50% $P_2O_5$.[113–14, 298] More readily filterable hemihydrate crystals are obtained by carrying out the initial attack in a layer of foam on the surface of the reaction slurry.[299] Another modification involves the conversion of the hemihydrate into anhydrite at 100° to 110°C. in 45 to 50% $P_2O_5$ acid containing 1 to 4% free sulphuric acid.[115–16] In others the hemihydrate originally formed is recrystallized separately to give gypsum of low phosphate content.[300, 301] Acid of 50% $P_2O_5$ concentration is obtained by heating sulphuric acid (98%) to 90° to 105°C., mixing with phosphate rock to form a stiff paste and then heating for about an hour at 200° to 240°C. The resulting clinker is extracted with weak phosphoric acid or water. About 60% of the fluorine is volatilized during mixing and increases to 88% on heating.[117] Fuming sulphuric acid (104%) has been used in a similar process to give acid of 50–55% $P_2O_5$ concentration.[299] Submerged combustion has been used to concentrate phosphoric acid to 70% $P_2O_5$ content.[118] The polyphosphoric acids thus formed are claimed to hinder or prevent the formation of base precipitates during subsequent ammoniation.[302]

The reaction between sulphuric acid and phosphate ores to produce fertilizers has been studied in very great detail. Many of the procedures used involve a curing stage in which the reaction mixture is allowed to stand so as to increase the amount of $P_2O_5$ extracted. The effects of time, temperature, acid ratio and concentration, and the particle size of the ore on the process have been studied.[108] Attempts to avoid the curing stage by air-drying the reaction mixture at temperatures up to 540°C. have not been very successful.[119] Sulphuric acid of 40 to 60% concentration is best for this procedure, but the conversion is only 90% as compared with 98% for conventional processes.[120]

### DECOMPOSITION OF PHOSPHORITES

Phosphorites are easier to decompose with sulphuric acid than are ores having an apatite structure. With a phosphorite complete decomposition occurred in 3 to 5 hr. at 20° to 30°C. and about 80% of the reaction took place in the first 10 min. To achieve a 95% conversion of apatite with the same acid, a temperature of 80°C. was necessary. On the other hand the phosphorite consumed 50 to 100% more sulphuric acid per ton of $P_2O_5$ than did the apatite. This was largely due to impurities, particularly iron, in the phosphorite. Gypsum of uniform and large crystal size was obtained only when the $SO_3$ and CaO concentrations in the liquid phase were 1 to 2·5% and 0·35 to 0·75%, respectively.[121]

In order to increase the amount of $P_2O_5$ extracted from phosphorites containing up to 10% $Fe_2O_3$, it is an advantage to calcine the ore at 1000°C. and carry out the extraction with acid at 35° to 40°C. Stirring for 2 to 4 hr. with 93% of the theoretical requirement of sulphuric acid gives 87% conversion of the $P_2O_5$. Addition of 5% of sodium or potassium chloride increases this to 95%, but the corresponding sulphates decrease the amount of $P_2O_5$ extracted.[122]

Some data on the reaction of sulphuric acid with low-grade phosphorites are given in Table I. These were obtained under conditions where the liquid/solid ratio in the reaction mixture was 2·5:1 to 3:1 and the $SO_3$ and CaO concentrations in the liquid phase were 1·5 to 2% and 0·3 to 0·7% respectively. The amount of sulphuric acid used is shown as a percentage of that required to convert the CaO in the ore into calcium sulphate.[123]

Sulphuric acid corresponding in composition to $H_2SO_4,H_2O$ has been used to decompose phosphorite, followed by neutralization with ammonia or urea.[124] Low-grade phosphorites have been treated with 15 to 20% sulphuric acid, or a mixture of this and ammonium sulphate, to give monoammonium phosphate. The residue, which is mainly gypsum, is suspended in water and treated with ammonia and carbon dioxide to recover the phosphorus.[125–6] Addition of ammonium sulphate to the sulphuric acid decreases the amount of base metals extracted from the ore and also increases the filtration rate. The most effective mixture contains 16 to 22% of ammonium sulphate. Amounts greater than this decrease the extraction of $P_2O_5$ as compared with sulphuric acid alone.[127] In a variation of this procedure, 83% of the acid is added within 10 min. and the remainder is then added as ammonium sulphate.[128] If the base metals in the phosphorite are 10% or more, decreased extraction of these occurs when the conversion of $P_2O_5$ is limited to 80%.[129]

*Table I.—Extraction of Phosphorites with Sulphuric Acid*

| Phosphorite composition | | $H_2SO_4$ used | Reaction conditions | | $P_2O_5$ extracted | Composition of $H_3PO_4$ produced | | | |
|---|---|---|---|---|---|---|---|---|---|
| % $P_2O_5$ | % metal oxides | % on CaO | Time hr. | Temp. °C. | % | % $P_2O_5$ | % $SO_3$ | % $Fe_2O_3$ | % $Al_2O_3$ |
| 21–22 | 11–12 | 110 | 6 | 75 | 60–80 | 18·5 | 4·5 | 2·0 | 1·3 |
| 24–25 | 8 | 110 | 6·5 | 75–80 | 85–87 | 22·5 | 4·5 | 1·7 | 1·3 |
| 24–25 | 8 | 105 | 4·5 | 75–80 | — | 19·6 | 5·6 | 3·9 | 1·4 |
| 18–19 | 3–6 | 105 | 3·5 | 65–75 | 92 | 20·5 | 4·8 | 2·4 | 0·9 |
| 18–19 | 3–6 | 105 | 3·5 | 70 | 93 | 22·5 | 5·0 | 2·5 | 1·0 |
| 18–19 | 3–6 | 97–100 | 1·5 | 60 | 96 | 13·5 | 1·4 | 1·1 | 0·5 |
| 24–25 | 8 | 97–103 | 6 | 75–80 | 94–97 | 23·5 | 2·6 | 2·0 | 1·0 |

The effect of heating phosphorites on their rate of solution in 5% sulphuric acid has been determined by means of differential thermograms at temperatures up to 1400°C. The maximum rate of reaction with acid occurs when the phosphorite has been heated to a temperature at which thermal breakdown of the crystalline lattice takes place with molecular rearrangement into new solid phases. Pyritized phosphorites require heating to below 700°C., glauconite ores to about 800°C., and carbonate–apatites to 1200° to 1300°C.[130]

The rate of reaction of phosphorites containing magnesium with sulphuric acid is higher in dilute slurries than in thick pulps. Variations in the amount of $P_2O_5$ extracted when the amount and concentration of sulphuric acid are altered have been attributed to the removal at higher acid concentrations of calcium sulphate which is deposited on the unchanged particles of phosphorite.[131–2] Increase in temperature lowers the rate of decomposition in dilute slurries but increases it in concentrated ones. This has been explained by changes in the degree of supersaturation of complexes in the reaction mixture with reference to the phases present in the $MgO–P_2O_5$ and $MgO–CaO–P_2O_5$ systems.[133] Observations on the further reaction which occurs during drying have been reported.[134]

## Decomposition with Phosphoric Acid

Phosphoric acid was first used in Germany in 1872 to extract phosphate ores for the production of fertilizer materials, particularly triple superphosphate.[135] In the earlier procedures the phosphoric acid was obtained by treating phosphate rock with sulphuric acid on the basis of the simple equation:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

This gave a dilute (20 to 30% $H_3PO_4$) phosphoric acid which was used to decompose a further quantity of the rock. One of the first developments of the process was to increase the acid concentration by drying the reaction mixture and allowing it to set. This was followed by a curing stage in which the mixture was allowed to stand, usually at room temperature. The effect of this was to improve the extraction and to make the $P_2O_5$ in the product more readily available to plants.[136]

More recently the trend has been towards the use of more concentrated sulphuric and phosphoric acids. In a typical procedure, Florida phosphate rock ($P_2O_5$ 31 to

33%, CaO 46 to 47%, F 3·5% and $Fe_2O_3 + Al_2O_3$ 1·7%) is treated with 93% sulphuric acid and the mixture cooled so as to maintain a temperature of 70° to 75°C. Calcium sulphate is removed by filtration and the phosphoric acid is concentrated by evaporation from 44 to 54% (32 to 39% $P_2O_5$). This acid is then treated at 80° to 100°C. with more phosphate rock of about 200 mesh-size, using an acid/rock weight ratio of 1·8. The water content is controlled to give a slurry which can be handled easily. In order to pass quickly through the plastic stage to the final free-flowing solid product, the reaction mixture is diluted with up to 20 times its weight of dust obtained from the later grinding stage. Successful operation depends largely on obtaining good crystals of gypsum in the sulphuric acid stage. This requires close control of the reaction time and temperature and of the acid concentration and the excess of acid used.[137]

Several processes have been worked out in which phosphorite or phosphate rock is caused to react in a single stage with a mixture of sulphuric and phosphoric acids. These give products varying in composition between that of ordinary and triple superphosphate. For any desired grade of product a suitable proportion of the two acids must be used. This complicates the selection of the best acid/phosphate ratio and raises the problem of the control of the amount of water in the reaction mixture. Graphs and other data enabling the appropriate acid composition to be calculated have been compiled.[138] Empirical equations have been derived which correlate the amount of acid with the phosphorus, calcium, iron, aluminium and fluorine contents of the rock.[139]

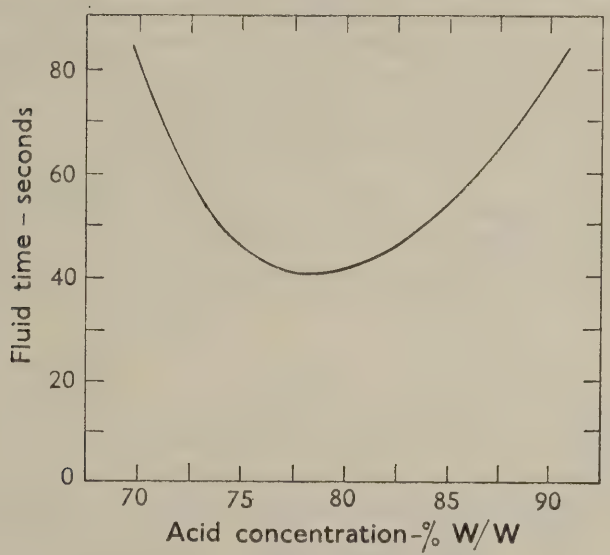

FIG. 4.—Effect of acid concentration on the fluid time in the reaction of phosphoric acid with Tennessee brown rock[143]

The duration of the curing stage is reduced from 4–6 weeks to 2–3 days by drying the reaction mixture at high temperatures.[119, 120, 140] If the acid reaction is carried out in an autoclave at 100° to 105°C. and the product then dried at 110° to 150°C., the curing time is as little as 10 hr.[141] The curing process is influenced by the acid concentration and the proportion of acid used.[142] These two variables are important in relation to several other factors involved in the phosphoric acid–phosphate rock reaction and many papers on the subject are to be found in the literature. Some of the more important data obtained in these studies are discussed below.

In the first stage of the reaction, immediately after mixing the rock with acid, the mixture is quite fluid. It then passes through a sticky, plastic stage, finally setting to a hard mass. The fluid time, as measured by determining the time for the reaction mixture to cease to flow in an inclined trough, is related to the phosphoric acid concentration as shown in Fig. 4. The data refer to Tennessee brown rock containing

33·4% $P_2O_5$, a reaction mixture having a $P_2O_5$/CaO molar ratio of 0·976, and the reactants initially at a temperature of 20°C. Somewhat different results are obtained with other types of rock and with different $P_2O_5$ contents, molar ratios and initial temperatures.[143, 142] The duration of the plastic stage is about 10% longer than the fluid time, and the time taken for the final solid to disintegrate to a powder is roughly equal to the plastic stage.[142, 144] If some of the phosphoric acid is replaced by an equivalent amount of sulphuric acid, the fluid time is shortened and the duration of the plastic stage increases.[144]

### EFFECTS OF CONCENTRATION OF PHOSPHORIC ACID

The most important effect of acid concentration is on the percentage conversion of the $P_2O_5$ in the rock to available $P_2O_5$. In the reaction of Tennessee brown rock (34·8% $P_2O_5$, 49·0% CaO) with phosphoric acid of concentrations between 60% and 80%, the percentage conversion varies as shown in Fig. 5. The theoretical requirement of acid is based on the $P_2O_5$ and CaO contents of the rock only and no allowance is made for the presence of iron, aluminium or other metals. The maxima in these curves are attributed to there being insufficient water in the system to enable complete conversion to occur during the 28 days' storage allowed in the experiments.[145, 142]

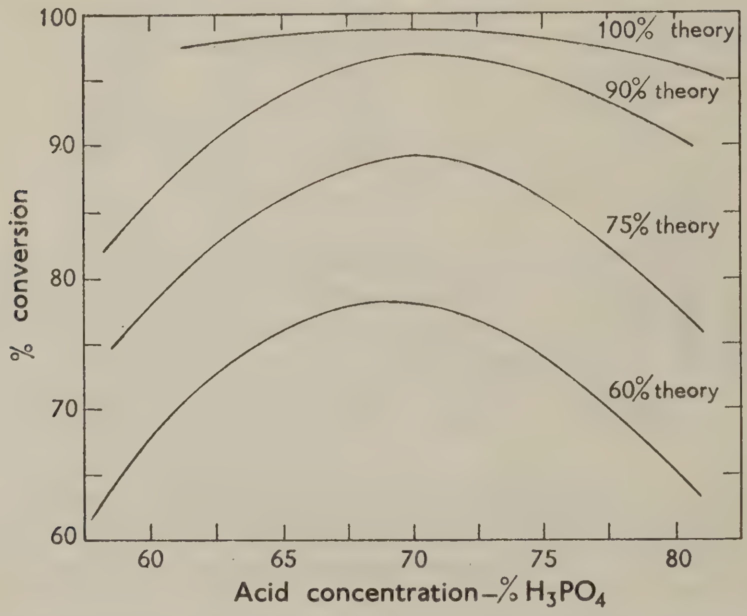

FIG. 5.—Effect of acid concentration on the reaction of Tennessee brown rock with phosphoric acid[145]

The behaviour of bone meal, bone ash, and Florida, Tennessee and Western States phosphate rock with phosphoric acid of various concentrations has been examined. So far as they can be compared, the results are substantially in agreement with those given above.[142–5] Florida rock is generally more reactive than other types of ore.[146]

The use of phosphoric acid of greater than 70% concentration has some practical advantages. The reaction with the rock becomes very rapid and sufficient heat is developed to dry the product during the curing period.[142, 144] If the reaction is carried out according to the equation:

$$3Ca_3(PO_4)_2,CaF_2 + 14H_3PO_4 + 10H_2O = 10Ca(H_2PO_4)_2,H_2O + 2HF$$

drying is not necessary because there is no excess of water in the system. This reaction corresponds to the use of 88% phosphoric acid.[144] Under these conditions a continuous mixing process is possible.[143, 142] On the other hand when acid of these high concentrations is used the influence of other factors such as temperature, particle size of rock and conditions of mixing becomes more marked. With acid containing less than 70% $H_3PO_4$ the temperature has only a minor effect on the percentage conversion of $P_2O_5$. At higher concentrations, however, low mixing and curing temperatures favour the conversion. Typical figures are increases in the percentage conversion from 62 to 74%, 76 to 92% and 83 to 96% when using 78% $H_3PO_4$ and the reactant temperature is decreased from 94° to 27°C. These improvements seem to be due to better mixing because of an increase in the duration of the fluid stage at the lower temperature. The lower temperature employed also decreases the amount of iron and aluminium extracted.[147] It is known that in the more concentrated acid systems aluminium, either alone or in the presence of iron, decreases the availability of the phosphorus in the product.[148–9] Iron alone, however, improves the citrate-solubility of the $P_2O_5$ because of the formation of complex calcium iron phosphates.[150, 151]

Phosphoric acid containing 76% $P_2O_5$ reacts rapidly with phosphate rock at about 100°C. and within 40 min. of mixing the temperature rises to 150° to 180°C. This volatilizes 60% of the fluorine in the rock as compared with 15% in conventional procedures. The product contains less than 1% of free water and the $P_2O_5$ is largely present as anhydrous monocalcium phosphate. The $P_2O_5$ content of the acid is equivalent to 105% $H_3PO_4$, but the actual composition is approximately 49% orthophosphoric acid, 42% pyrophosphoric acid and 9% of higher polyphosphoric acids. The percentage conversion of Florida rock (32% $P_2O_5$) with this acid is only 65% but this increases to 86% for 103% $H_3PO_4$, 92% for 102% $H_3PO_4$ and remains constant at 90% with 98 to 101% $H_3PO_4$.[152]

By dissolving phosphate rock with an excess of phosphoric acid in this way, a defluorinated solution can be obtained, from which solid monocalcium phosphate can be crystallized. The salt can be converted to phosphoric acid of good quality by treatment with ion exchange resin.[303]

### RATE OF THE REACTION

The rate of reaction of phosphoric acid with apatite and phosphorites under various conditions has been measured. At 40° to 100°C. apatite dissolves slowly in saturated solutions of dicalcium phosphate and the rate slows down to zero as the reaction products are deposited on the unreacted apatite. A similar phenomenon occurs in monocalcium phosphate solutions, but a thicker layer of deposit is required to inhibit the reaction. At 40°C. the rate of solution increases with the $P_2O_5$ content of the system, but the reverse occurs at 75°C.[153] The rate of solution is a function of the viscosity of the solution and the hydrogen ion activity.[154] The rate of decomposition of apatite by phosphoric acid is reported to be proportional to the hydrogen ion concentration and the surface area of the mineral and also to be a logarithmic function of the reciprocal of the absolute temperature.[155] Graphs and other data relating the decomposition rate with acid concentration have been given.[156]

Data for the rate of dissolution of apatite in aqueous mixtures of phosphoric acid (35–40%) and sulphuric acid (0–4%) suggest that slow dissolution results from nucleation of $CaSO_4,\frac{1}{2}H_2O$ on the surface of the rock particles. This was related to the degree of supersaturation, defined as the ratio of apparent to equilibrium solubility product constants. With a ratio close to 1, no nucleation of hemihydrate occurs; as the ratio approaches 2·5 hemihydrate precipitates but the apatite is completely dissolved. For ratios higher than 2·5 the coating of hemihydrate retards dissolution of the rock.[304]

In another investigation the rate of decomposition ($k$) of apatite by phosphoric acid was found to increase with the acid concentration and the temperature only during the first few minutes of the reaction. As the initial acid concentration increased, $k$ passed through a maximum, and by using sufficiently concentrated acid the reaction could be inhibited completely. It appears that a dense film of reaction products is formed on the surface of the undecomposed apatite and that in the later stages the reaction rate is controlled by the rate of diffusion of phosphoric acid through this film.[157] The rate of decomposition of apatite at 20° to 60°C. has been found to decrease from 66% conversion during the first hour to a 4% conversion in the second.[158] The optimum phosphoric acid concentration is 54 to 55% $P_2O_5$.[159, 158]

Similar phenomena have been observed in the reaction of magnesium-containing phosphorites ($P_2O_5$ 27%, CaO 43%, MgO 3% and $CO_2$ 8%) with phosphoric acid. A maximum decomposition rate at 20°C. occurs with acid containing 54% $P_2O_5$, and the initial high reaction rate falls off as the reaction products are deposited on the unreacted ore.[160] Phosphorites containing large proportions of carbonate give a porous, powdery material when they react at 50° to 55°C. with phosphoric acid. This differs from the dense, plastic mass obtained with apatite and is due to evolution of carbon dioxide during the acid treatment.[161] With glauconitic phosphorites the initial decomposition rate is proportional to the hydrogen ion concentration, but decreases as the reaction proceeds, owing to deposition of silica on the unchanged ore.[162] Other types of phosphorite are rapidly decomposed by 20% phosphoric acid at 20°C. and the rate does not seem to be affected by the geological characteristics of the phosphorite.[163]

### PERCENTAGE CONVERSION

For any given acid concentration the percentage conversion of $P_2O_5$ in phosphate rock is generally increased by using a greater proportion of acid. The effect is shown in Fig. 6 for three concentrations of acid, using a rock containing $P_2O_5$ 28%, CaO 39%, $SiO_2$ 13%, $Al_2O_3$ 6%, $Fe_2O_3$ 2%, F 3·2% and $CO_2$ 1·2%.

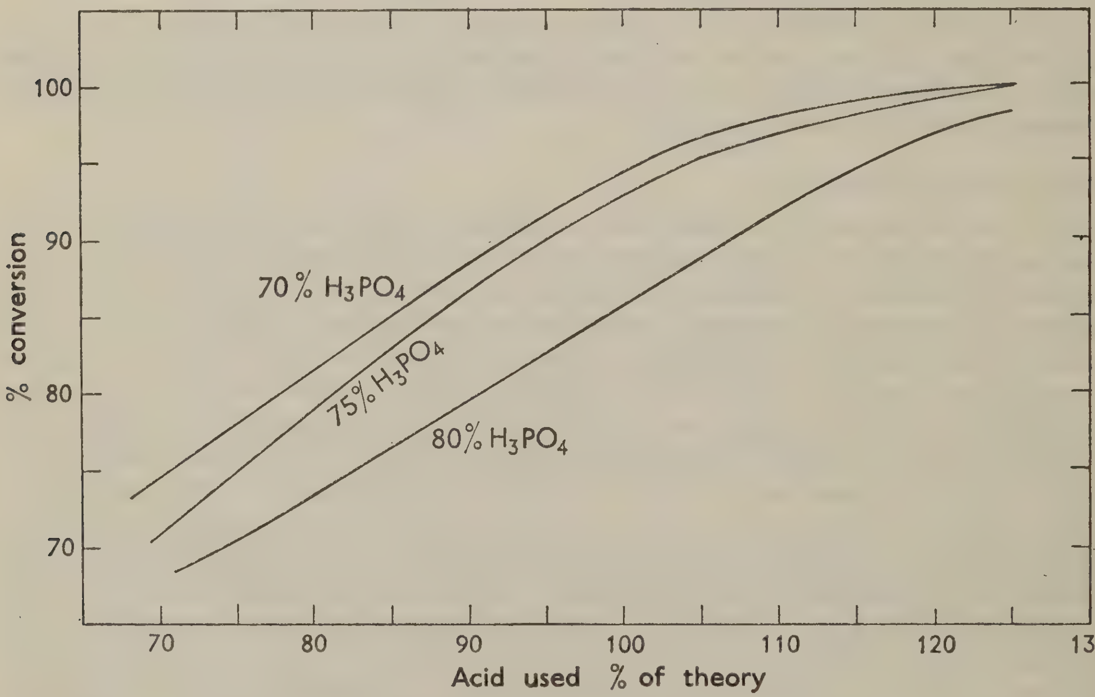

FIG. 6.—Effect of proportion of acid on the reaction of Tennessee brown rock with phosphoric acid[145]

The theoretical quantity of acid is calculated only on the $P_2O_5$ and CaO content of the rock and takes no account of the iron and aluminium present.[145] Similar results have been reported for Tennessee rock containing 35% $P_2O_5$ when reacted with 47% phosphoric acid.[146] The effect with Florida rock (32% $P_2O_5$, 46% CaO) and 102% phosphoric acid (74% $P_2O_5$) is shown in Fig. 7. The reactants were mixed at 65°C. and the $P_2O_5$/CaO ratio refers to the total $P_2O_5$ (i.e. that in the rock and in the added acid) to CaO in the reaction mixture.[152]

The ratio of acid to rock in the reaction mixture has a relatively minor influence on the fluid and setting times. Excess of acid increases these times and also improves the conversion slightly.[142–5]

Decrease in the particle size of the rock has a marked effect on the fluid time as shown in Fig. 8.[143]

There are somewhat conflicting reports on the influence of temperature on the reaction of phosphoric acid with phosphate rock, particularly as regards the percentage conversion to available $P_2O_5$. The initial temperature of the reactants affects the fluid time as shown in Fig. 9.

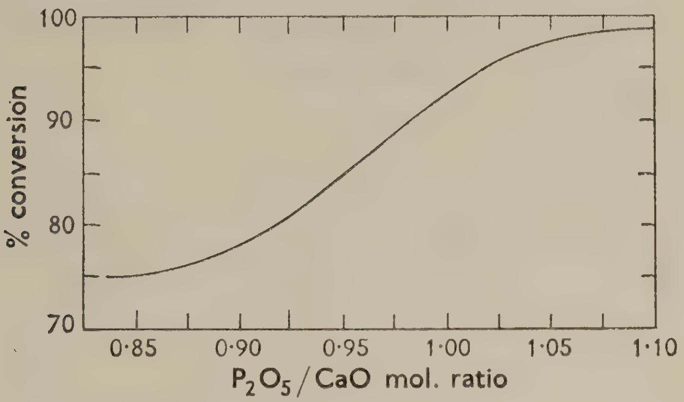

FIG. 7.—Effect of acid ratio on the reaction of Florida rock with 102% phosphoric acid

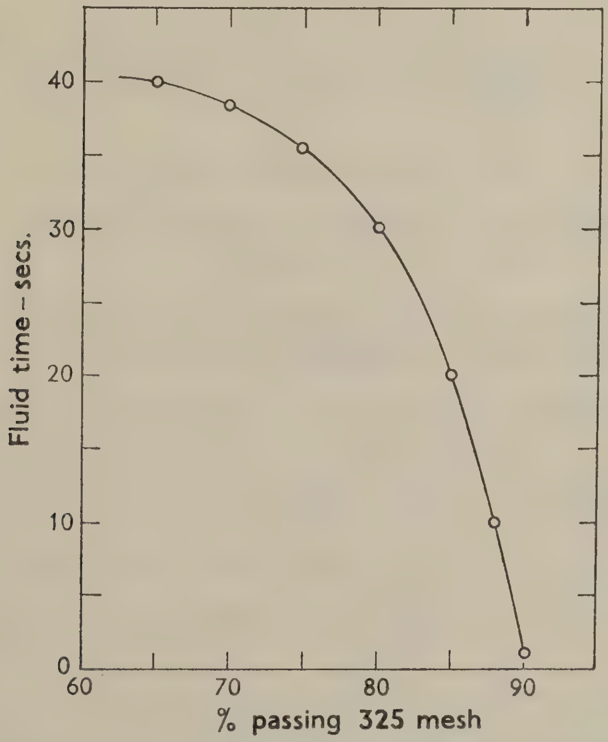

FIG. 8.—Effect of particle size on the fluid time in the reaction of Tennessee brown rock with 78% phosphoric acid[143]

Increasing the initial temperature of the reaction from 20° to 60°C. is said to improve the conversion by 2 to 12% when phosphoric acid of 21 to 64% concentration is used.[146] With 74 to 78% acid no effect on the conversion was found at 20° to 77°C.[144] Reaction of Florida rock with 102% phosphoric acid gave a conversion of 83% at 50°C., increasing to 90% at 90°C. and remaining constant at 90% for temperatures up to 150°C.[152]

It has also been reported[147] that the initial reaction temperature has little effect on the percentage conversion when the phosphoric acid concentration is 70% or less. At higher acid concentrations low reactant temperatures and low curing temperatures appear to favour the conversion. Some data illustrating this are shown in Fig. 10.

The contradictory nature of these results may be due to other factors having an influence on the experimental data. For example, calcium fluoride in the product can cause reversion of the phosphate to an unavailable form and this reaction is favoured by high curing temperatures. Evolution of fluorine and the extent of reaction of iron and aluminium in the rock are influenced by experimental conditions and these affect the citrate-solubility of the product.[145]

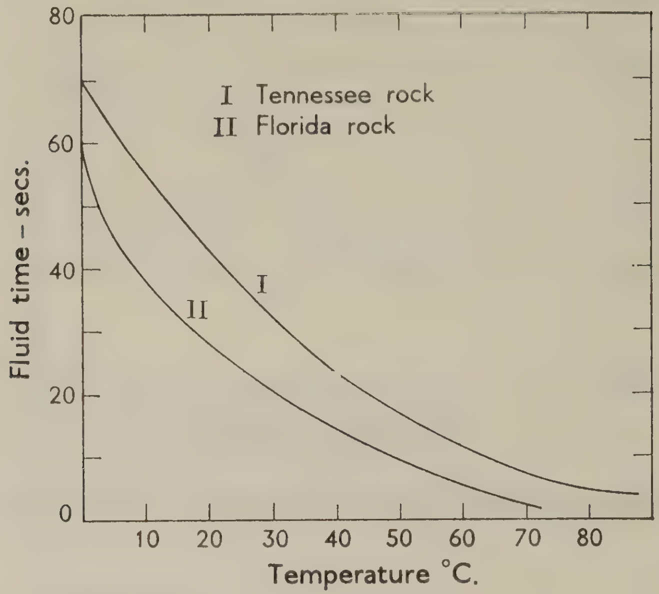

FIG. 9.—Effect of initial temperature on the fluid time in the reaction of Tennessee and Florida rock with phosphoric acid[143]

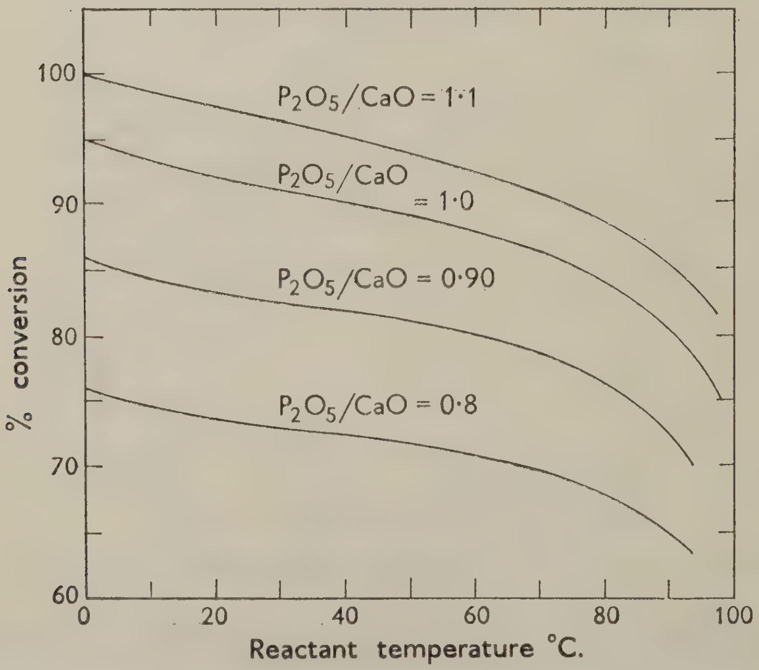

FIG. 10.—Effect of initial reactant temperature on the reaction of Tennessee brown rock with 78% phosphoric acid at various acidulation ratios[147]

A high $P_2O_5$ content in the phosphate rock favours the conversion to citrate-soluble phosphorus. The effect is shown in Fig. 11 for 70% phosphoric acid at five different acidulation ratios. The theoretical quantity of acid is based on the $P_2O_5$ and CaO in the rock, with no allowance for iron and aluminium. For the rock used an excess of about 20% of acid was sufficient to react with all the iron and aluminium present. This accounts for the difference between the results shown in Fig. 11 and Fig. 6 for the amounts of acid required for complete conversion of the rock. The higher grade ore contains less iron and aluminium, so that a smaller amount of acid is required for complete reaction.[145] For more precise details of the experimental conditions, type of rock used and other factors affecting the reaction, the original papers referred to above should be consulted.

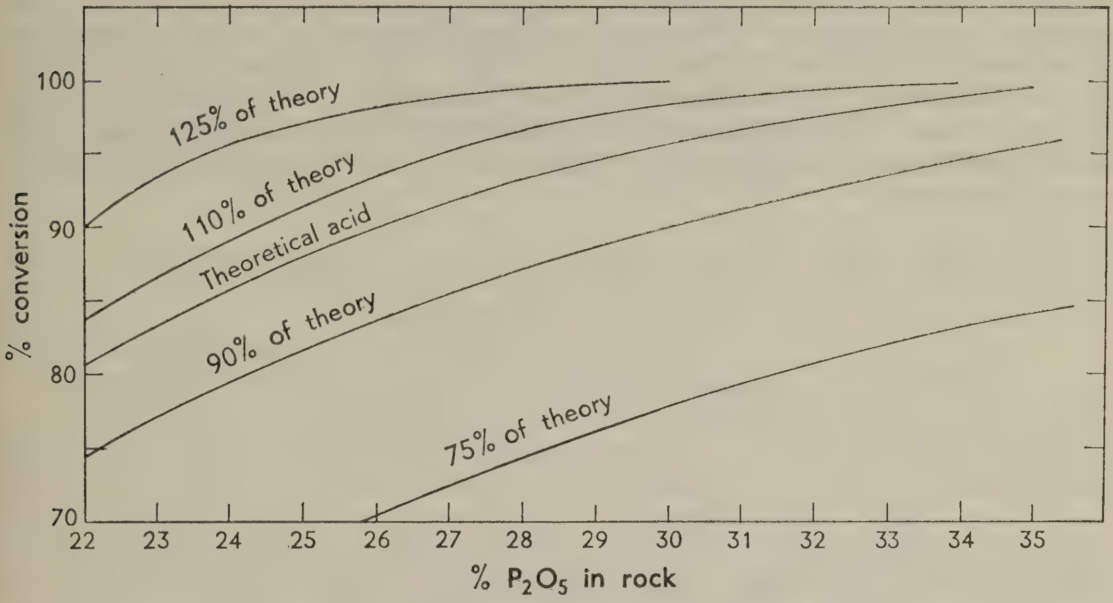

FIG. 11.—Influence of the $P_2O_5$ content of Tennessee brown rock on its reaction with 70% phosphoric acid[145]

In a common procedure for extracting phosphate rock and phosphorites, the ore is caused to react with sulphuric or phosphoric acid according to the equations:

$$3Ca_3(PO_4)_2,CaF_2 + 6H_2SO_4 = 3Ca(H_2PO_4)_2 + 6CaSO_4 + CaF_2$$
$$3Ca_3(PO_4)_2,CaF_2 + 12H_3PO_4 = 9Ca(H_2PO_4)_2 + CaF_2$$

If the extraction is carried out under conditions such that only dicalcium phosphate is formed, the amount of acid required per unit weight of ore is considerably reduced. The equations for these reactions are:

$$3Ca_3(PO_4)_2,CaF_2 + 3H_2SO_4 = 6CaHPO_4 + 3CaSO_4 + CaF_2$$
$$3Ca_3(PO_4)_2,CaF_2 + 3H_3PO_4 = 9CaHPO_4 + CaF_2$$

Earlier attempts[164] to carry out these reactions were unsuccessful because deposition of dicalcium phosphate on the unreacted rock inhibited the reaction. More recently, however, it has been found that under suitable conditions monocalcium phosphate reacts with water according to the equation[166]:

$$Ca(H_2PO_4)_2,H_2O + xH_2O = CaHPO_4 + H_3PO_4 + (x+1)H_2O$$

This reaction is dependent on the amount of water in the system and at 100°C., for example, 80% conversion to dicalcium phosphate occurs when there are 28 g. of water present per 100 g. of monocalcium phosphate monohydrate.

Formation of dicalcium phosphate occurs when sulphuric or phosphoric acid is added to phosphate rock in amounts sufficient to convert only part of it into monocalcium phosphate, and the reaction mixture is heated for a short time at 110°C. under reflux, and then at 185°C. without refluxing. The percentage conversion on heating phosphate rock with 1·77 times its weight of monocalcium phosphate monohydrate for 15 min. at 110°C., followed by 30 min. at a higher temperature, is shown in Fig. 12.

Heating for longer than 30 min. at 185°C. has no effect on the conversion, but under these conditions the ratio of monocalcium phosphate monohydrate to phosphate rock has a marked influence. The conversion decreases from 98% when the weight ratio is 1·77 to 60–70% when it is 0·6.[167]

In the extraction of phosphorites with phosphoric acid, all the phosphorus and a minimum amount of silica, iron and aluminium are removed if the ore is first heated for 2 hr. at 1050°C. and then reacts with the acid for 1 hr. at 80°C. Addition of sulphuric acid to the mixture decreases the amount of iron and silica extracted but increases the aluminium.[168] Magnesium in the phosphorite is also extracted by phosphoric acid, but the $MgO–P_2O_5–H_2SiF_6–H_2O$ phase diagram at 25°C. shows that the magnesium can be removed as the silicofluoride.[169] A practical application of this reaction has been described, in which $MgSiF_6,6H_2O$ is precipitated. It is removed and heated with phosphoric acid at 300° to 350°C. to recover $SiF_4$ and HF which are re-used.[170]

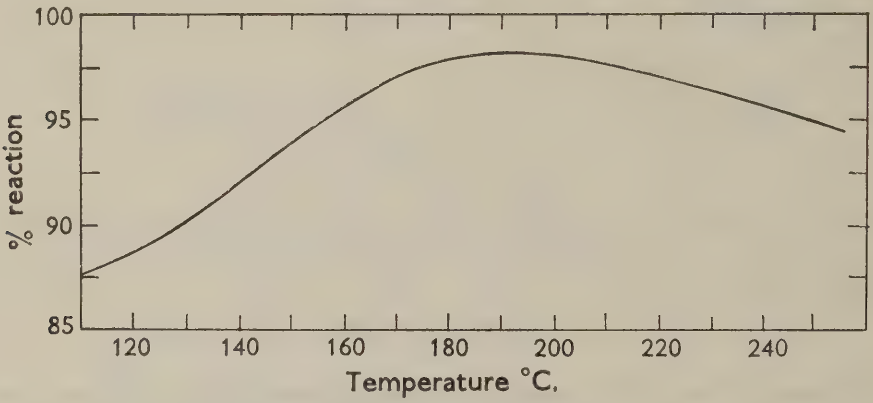

FIG. 12.—The effect of temperature on the reaction of monocalcium phosphate with Florida phosphate rock[167]

A study has been made of schemes for the preparation of concentrated phosphoric acid by decomposition of apatite with a mixture of hydrofluoric and hexafluorosilicic acid:

$$Ca_5F(PO_4)_3 + 9HF(+H_2O) \rightarrow 5CaF_2 + 3H_3PO_4(+H_2O)$$
$$Ca_5F(PO_4)_3 + 5H_2SiF_6(+3H_2O) \rightarrow 5CaSiF_6,2H_2O + 3H_3PO_4 + HF(+H_2O)$$

Phosphoric acid obtained by attacking apatite with technical HF (33% HF, 5% $H_2SiF_6$) for 30 min. at 100°, contained 45–48% $H_3PO_4$, 0·3–0·6% CaO and 5–8% F.[305]

A summary up to the year 1933 has been made of the various methods of decomposing phosphate ores with mineral acids and of processes for converting these into materials of commercial value.[171, 165]

### Decomposition with Alkalis

Several methods of extracting phosphate ores under alkaline conditions have been proposed, but these are generally much less efficient as commercial processes than the acid procedures described above.

In one method phosphate rock ground to pass 70-mesh is mixed with 50% aqueous sodium hydroxide in proportions to give a molar $NaOH/P_2O_5$ ratio of 5 and is then heated under pressure for 1 hr. at 200°C.[172] Similar results are obtained when part of the sodium hydroxide is replaced by sodium silicate in the proportion of 0·2 to 0·5 mols. $SiO_2$ per mol. of CaO in the rock.[173–4]

Other processes involving the use of alkalis at higher temperatures are described below (see page 93).

## Decomposition by Chlorination

Low-grade phosphorites can be decomposed by heating a mixture of three parts of ore and one part of wood charcoal for 2 hr. at 700° to 800°C. in a rapid stream of chlorine, the gaseous products being absorbed in water. About 97% of the phosphorus is recovered, together with about half of the iron and aluminium in the phosphorite.[175] Absorption of the gases in ammonia solution increases the yield.[176] Addition of 5% of nickel chloride or copper sulphate to the reactant mixture decreases the reaction time from 10 to 3 hr. and lowers the temperature from 800°C. to 650–700°C.[177] The presence of a small percentage of water in the mixture increases the reaction.[178]

Chlorination more than doubles the fertilizing action of ground phosphorite, making it at least as effective as superphosphate in this respect. The improvement over untreated, ground phosphorite is attributed to the decomposition by the chlorine of the calcium carbonate present in the ore.[179] As a result the pH of aqueous extracts of treated material is 3 to 3·5 whereas extracts of the original phosphorite have pH 6·5 to 7·0. This increase in acidity favours the assimilation of $P_2O_5$ by plants.[180] Treatment of phosphorites with chlorine or hydrogen chloride at high temperature removes all of the carbon dioxide, some of the fluorine and most of the base metal oxides. Chlorinated phosphorites are generally more effective as fertilizers than those treated with hydrogen chloride,[181] perhaps because their $P_2O_5$ content is higher as well as being more available to plants.[306]

Phosphorus pentachloride has been obtained by complete chlorination of low-grade phosphorite in the temperature range 600° to 1200°C. in the presence of carbon. The extent of the reaction depends on the temperature, the rate of flow of chlorine, the amount of carbon used and the moisture content of the system. Under the best conditions 85% of the phosphorus in the ore is extracted.[182] In the presence of salt and carbon, phosphorites are chlorinated to phosphorus oxychloride and phosphorus trichloride in the temperature range 600° to 800°C.[183] Phosphorus oxychloride only is said to result from the chlorination at 600° to 650°C. of a mixture of phosphate rock and carbon with 0·5 to 1·0 parts of sodium chloride.[184] The yield from this reaction is very variable and is influenced by the composition of the phosphate rock. For example, 80 to 90% of the phosphorus is extracted when chlorine at 650° to 670°C. is passed over briquets made from tar, charcoal and fluorapatite, but only 65% can be recovered as phosphorus oxychloride. The low yield may be due to hydrolysis of the phosphorus oxychloride by moisture in the system, according to the equation:

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl$$

Phosphorus oxyfluoride may be formed, and Van Wazer,[83] considers that under the above conditions the reaction approximates to the equation:

$$3[3Ca_3(PO_4)_2,CaF_2] + 27C + 54Cl_2 = 16POCl_3 + 2POF_3 + 30CaCl_2 + 27CO_2$$

The chlorine efficiency of this process is low because of wastage through its conversion into calcium chloride and chlorides of the base metals present in the phosphate rock, e.g. iron and aluminium.[185]

In a variation of the above procedure, a mixture of equal parts of finely-ground phosphate rock and ground coal is heated at 500°C. in sufficient chlorine for complete conversion of the rock to calcium metaphosphate. The product is then heated for a further period at 600° to 750°C., in a lower concentration of chlorine, to yield phosphorus oxychloride as the final product.[186]

A more complicated and less practical procedure has been described. This involves the formation of phosphoric acid from phosphate rock and sulphuric acid followed by reduction and chlorination.[187]

Chlorine has been used in conjunction with sulphur dioxide by passing the gas into a suspension of phosphorite in a solution containing 7 to 8% $SO_2$. An 85% decomposition of the phosphorite is obtained at ordinary temperature and pressure.[188]

This is essentially a reaction of the phosphorite with sulphuric and hydrochloric acids formed according to the equation:

$$SO_2+Cl_2+2H_2O = H_2SO_4+2HCl$$

The same two gases may be passed into a slurry of phosphate rock in a solution of sodium sulphate to give phosphoric acid, sodium chloride and calcium sulphate.[189] A suspension of ground phosphate rock in 46% phosphoric acid has also been subjected to the action of chlorine and sulphur dioxide for 3½ hr. at 95°C.[190]

Sulphur monochloride reacts exothermically with phosphorites at room temperature. On average, 75% of the sulphur in the monochloride is reduced to elemental sulphur and the remainder is oxidized to sulphuric acid. After reaction for 24 hr. over 95% of the phosphorus is recovered. The mechanism proposed for the reaction is:

$$\begin{aligned} 2Ca_3(PO_4)_2+6S_2Cl_2 &= 6CaCl_2+2P_2O_5+3SO_2+9S \\ SO_2+Cl_2+2H_2O &= H_2SO_4+2HCl \end{aligned}$$

In the presence of excess of sulphur monochloride the phosphorus pentoxide formed is converted into phosphorus oxychloride.[191]

Phosphorites react with a mixture of chlorine and carbon monoxide in the presence of carbon as a catalyst. The reaction starts at 180°C. and is rapid at 350°C.; the overall equation is:

$$Ca_3(PO_4)_2+6CO+6Cl_2 = 2POCl_3+6CO_2+3CaCl_2$$

The evidence is, however, that two stages are involved; calcium metaphosphate is formed at the lower temperatures:

$$Ca_3(PO_4)_2+2CO+2Cl_2 = Ca(PO_3)_2+2CO_2+2CaCl_2$$

further reaction at higher temperatures then converts this into phosphorus oxychloride[192]:

$$Ca(PO_3)_2+4CO+4Cl_2 = 2POCl_3+4CO_2+CaCl_2$$

Similar reactions occur at 350° to 500°C. when minerals such as vivianite and pyromorphite are heated in a stream of phosgene. This reaction may be written as[193–4]:

$$3MO,P_2O_5+6COCl_2 = 2POCl_3+6CO_2+3MCl_2$$

At 800°C. uranium can be separated as uranium tetrachloride from uranite by the reaction[194]:

$$CaO,2UO_2,P_2O_5+8COCl_2 = 2POCl_3+2UCl_4+8CO_2+CaCl_2$$

The treatment of phosphorites with chlorine, hydrogen chloride, sulphur chlorides and carbon tetrachloride has been discussed.[195]

### Decomposition by Thermochemical Methods

Many investigations have been made into thermal methods of improving apatites and phosphorites. These processes are usually carried out at temperatures above 1000°C. and give rise to so-called thermophosphates. The latter are generally used as fertilizers and the aim of the thermal treatment is to render the phosphate available to plants and to increase the agricultural value of the product by incorporating in it elements which enhance the fertilizing action. This applies particularly to phosphorus ores which are of too low a grade to be worth converting to phosphoric acid or extracting by the methods described above. Some ores, even though they have a reasonably high content of phosphorus, also contain quantities of silica, base metals and other impurities which are difficult to remove chemically from the final product. In some instances it is possible to combine thermal and other processes to give phosphates and other products of commercial value.

Direct application to the soil of ground phosphate minerals is not always very successful as regards crop response. The action as a fertilizer depends largely on the mineralogical composition of the ore. In general, phosphates with a fluorapatite structure are more difficult for plants to assimilate than phosphorites or minerals of mixed composition such as kurskite, $2Ca_3(PO_4)_2,CaCO_3,CaF_2$.[196] Fine grinding may increase the amount of phosphate assimilated,[197] but the degree of fineness is chiefly determined by the petrographic composition of the ore.[197] The solubility of the phosphate in water is usually of importance in determining crop response, which is much less marked in calcareous soils[198] and those having a low moisture content. This effect is often measured by determining the solubility of the phosphate in solutions of citric acid or ammonium citrate. The latter gives low results, indicating poor availability of phosphorus to the soil, and for this reason a 2% solution of citric acid is more often used as a standard test. Even though fluorapatite is almost insoluble in 2% citric acid, the test is not always satisfactory. In some instances plant growth tests show that less phosphate is available than is indicated by the citric acid solubility of the phosphate. The concentration of the citric acid, time of contact of phosphate with it and the proportion of solid to liquid have been shown to be relevant factors in the results given by the test.[199]

Heat treatment of phosphate rock at temperatures below 1000°C. is usually carried out to improve the grade of the mineral and its ease of grinding, and to remove organic matter and carbonate which adversely affect its behaviour on acidulation. The response to calcination depends on the variety of rock treated. Thus Moroccan phosphate showed a sharp collapse of the internal structure of its particles between 500° and 700°C. which was less evident in Utah phosphate. Solubility of phosphorus decreased in the Moroccan rock, but reached a maximum at 850° in the Utah rock. The reactivity of both rocks was somewhat decreased by calcination.[307] A Florida rock phosphate after heating at 1000° showed a similar decrease in acid solubility, accompanied by an increase in apatite crystal size, and a disappearance of crystalline quartz.[308]

Phosphorites are quite reactive towards a number of substances at temperatures above 1000°C., the reactivity being increased in the molten state. Fusion processes usually convert the phosphate into a metastable state. If the structure of the high-temperature form can be preserved at ordinary temperatures the product generally becomes more reactive than it was before melting. To achieve this, quenching or rapid cooling is necessary and the rate of cooling depends on the nature of the product being made. Quenching of the product may be more important than its actual chemical composition. The latter may be varied over a wide range with only gradual changes occurring in the physical and chemical properties of the thermophosphate. The three most important methods of heating phosphates are sintering in a rotary kiln, melting in a cyclone furnace and sintering in a fluidized bed.[309–10]

It has been shown that if apatite or phosphorite is fused with quartz sand and magnesium oxide or serpentine and the product is cooled slowly, less than 4% is soluble in 2% citric acid. The material is essentially crystalline with a structure similar to that of fluorapatite. Rapid cooling produces a material which is a glass and is completely soluble in citric acid.[200]

Thermal methods of decomposing phosphorites may be divided into acid and basic processes. In the acid process phosphorite is mixed with up to 37% of its weight of silica in the form of sand and is then heated to over 1400°C. and cooled rapidly. Over 98% of the $P_2O_5$ is soluble in citric acid. In the basic processes alkaline materials are mixed with the phosphorite. This method is generally more efficient than the acid procedure and the reaction temperature is lower. With potassium minerals such as feldspar and phonolith the reaction occurs at 1100° to 1200°C. and can be represented by the equation:

$$Ca_3(PO_4)_2 + K_2O = K_2Ca_2(PO_4)_2 + CaO$$

The amount of alkali used should be approximately one mol. of $K_2O$ for one mol. of $P_2O_5$ in the phosphorite.[201] Mixtures of phosphorite and calcium carbonate with sodium carbonate or sodium sulphate may also be sintered at 1200°C. in a current of steam.[202] Processes in which coal is added and the alkali is replaced by magnesium oxide have been used.[203] Substitution of sodium chloride for sodium carbonate is successful only if coal is also added. With some types of phosphorite sodium carbonate is reactive at temperatures as low as 700° to 800°C.[204]

Sintering of phosphate ores rather than fusion has been developed as a commercial process to give the so-called Rhenania phosphates. In this process the ore is mixed with sodium carbonate to give a molar $Na_2CO_3:P_2O_5$ ratio of unity and sufficient silica is added to form calcium silicate with the calcium oxide in the phosphate. The materials are finely ground, 10% of water is added and the mixture is heated for about 2 hr. in a rotary kiln at 1000° to 1200°C. Very little fluorine is volatilized in the process.[205]

The reaction of sodium carbonate with phosphorites has been studied for three different phosphorus contents, the extent of decomposition being measured by the amount of the product which was soluble in citric acid. The results are summarized in Table II.

*Table II.—The Reaction of Phosphorites with Sodium Carbonate at* 900° *to* 1300°*C.*[206]

| Temp. °C. | % $P_2O_5$ in ore | Parts $Na_2CO_3$ per 100 ore | % decomposition |
|---|---|---|---|
| 900–1200 | 40 | 30 | 70 |
| | 40 | 37·5 | ~85 |
| | 40 | 45 | ~85 |
| 1100 | 40 | 45 | 61 |
| 1200 | 40 | 45 | 93 |
| 1300 | 40 | 45 | 93 |
| 900 | 27 | 25 | 82 |
| 1100 | 27 | 20 | 75 |
| 1100 | 27 | 25 | 100 |
| 1100 | 19·5 | 22 | 100 |

The maximum solubility in citric acid is achieved by fusing the ore for 30 min. at 1100° to 1200°C. with a weight of sodium carbonate equal to 110% of the $P_2O_5$ in the ore.[206]

Sintering at 800° to 1300°C. of a mixture of apatite with 1 to 6 mol. of sodium carbonate per mol. of $P_2O_5$ has been proposed. The product is extracted at 80°C. with a solution saturated with sodium carbonate at 65° to 70°C. and containing a small proportion of sodium hydroxide.[207] According to Van Wazer,[83] the leaching stage is critical in this process. If the solution contains more than 4% $P_2O_5$ then the forward reaction:

$$(CaO)_{3-x}(Na_2O)_xP_2O_5 + (3-x)Na_2CO_3 \rightarrow 3CaCO_3 + 2Na_3PO_4$$

is opposed by the reverse one between calcium carbonate and trisodium phosphate:

$$3CaCO_3 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3Na_2CO_3$$

A similar process using sodium hydroxide alone and operating at 400°C. has been described.[208]

Sulphates have been used in the thermal decomposition of phosphate ores. Apatite, mixed with silica, carbon and sodium sulphate is fused at 1250°C. in an atmosphere of carbon dioxide or nitrogen. A product containing $Ca_2SiO_4$, $Na_2SiO_3$ and $CaNaPO_4$ is obtained.[209] In another procedure a mixture of phosphate rock and ammonium sulphate is heated at 450° to 515°C. and the product is leached with water. The calcium sulphate residue is treated with carbon dioxide, ammonia and water to recover ammonium sulphate which is re-used.[210]

If apatite is sintered at 1100° to 1200°C. with potassium sulphate and charcoal the product has all its phosphorus in an available form. In the presence of air the reaction may be represented by the equation:

$$3Ca_3(PO_4)_2,CaF_2 + 4K_2SO_4 + 8C + 6O_2 = 6CaKPO_4 + 2KF + 4CaO + 8CO_2 + 4SO_2$$

Less sulphate is required, and the $P_2O_5$ content of the product is increased, if water vapour is passed over the mixture. Under these conditions the reaction is:

$$3Ca_3(PO_4)_2,CaF_2 + 3K_2SO_4 + 6C + 4H_2O = 6CaKPO_4 + 2HF + 4CaO + 3H_2S + 6CO_2$$

The most favourable conditions, which give a 96% decomposition of the phosphorite, are sintering for 30 min. at 1100°C. in the presence of water vapour, using a mixture of four parts of phosphorite, two of potassium sulphate and one of charcoal.[211]

In a similar procedure[212] a mixture of equal parts of phosphorite and astrakhanite ($Na_2SO_4,MgSO_4,4H_2O$) and 40% of coal is heated at 1250°C., or is melted at 1400°C. in a reducing atmosphere and is then quenched.[213]

Potassium sulphate alone does not react with apatite under these conditions. Since carbon is necessary for the reaction it is assumed that the intermediate formation of potassium sulphide is involved.[214] A similar mechanism is postulated for the reaction with sodium sulphate and carbon at 800°C. according to the equation[215]:

$$Ca_3(PO_4)_2 + 2Na_2SO_4 + 8C = CaNaPO_4 + Na_3PO_4 + 2CaS + 8CO$$

Magnesium sulphate on the other hand reacts only in the absence of carbon according to the equation[214]:

$$3Ca_3(PO_4)_2,CaF_2 + 9MgSO_4 + H_2O = 3Mg_3(PO_4)_2 + CaO + 9CaSO_4 + 2HF$$

When carbon is present in this reaction an unstable magnesium sulphide is formed and this rapidly decomposes into the oxide, sulphur dioxide and hydrogen sulphide.

The reactions between Florida phosphate rock and magnesium and potassium sulphates and the minerals langbeinite ($K_2SO_4,2MgSO_4$) and polyhalite ($K_2SO_4, MgSO_4,2CaSO_4,2H_2O$) have been examined in some detail. Mixtures of these were melted at 1150°C. and were then quenched, the extent of the reaction being determined by citric acid solubility of the product. The results, shown in Fig. 13, indicate that potassium sulphate is much less reactive than the magnesium salt, while polyhalite occupies an intermediate position.[216]

The reaction between phosphate rock, magnesium oxide and silica has also been studied carefully. Quenching of melts prepared at 1450° to 1550°C. gives products containing up to 99% of citrate-soluble phosphorus. The mineral olivine ($SiO_2$ 44%, MgO 45%, $Fe_2O_3$ 8%) may be substituted for the magnesium oxide–silica mixture.[217]

At 1500°C. apatite and the mineral serpentine ($Mg_3H_4Si_2O_9$) react to form magnesium pyrophosphate, with complete elimination of fluorine from the rock.[218]

Other magnesium minerals, such as dolomite and magnesite, have been considered as reagents for producing thermophosphates from phosphorites.[219] The fertilizing value of magnesium thermophosphates has been shown to be comparable with that of superphosphate, particularly on acid soils.[220] On the other hand there is evidence that this is related to the fluorine content of the product and the conditions of treatment of the phosphate. The reaction between apatite and magnesium oxide in the absence of silica at high temperature does not remove the fluorine. In the presence of both, the magnesium oxide gives readily fusible compounds, and the silica assists diffusion in the melt and aids the elimination of fluorine as silicon tetrafluoride.

Slow cooling of the melt when fluorine is present causes reversion to fluorapatite and reduction in the availability of phosphorus in the product. Quenching of the material from the molten state largely avoids this. It also prevents the transformation, which occurs at 1100°C., of tricalcium phosphate into a modification in which the phosphorus is not biologically available. In the presence of excess of calcium, together with silica, no quenching is necessary because the resulting calcium silicophosphate does not undergo polymorphic transformation on cooling. Citrate-soluble products are obtained by simple fusion and quenching if the apatite contains the correct proportions of magnesium oxide and silica.[221]

The effects of temperature and the amount and nature of the materials added to the reaction mixture on the available phosphate have been studied for apatite and a phosphorite. Only 30% of the phosphorus becomes available when apatite ($P_2O_5$ 40%, CaO 52%, F 3·2%) is fused at 1800°C. with lime and/or silica and is not quenched. Almost complete availability occurs when the melt is quenched, even though only 10% of the fluorine is volatilized. Similar results were found with an apatite–nepheline ore ($P_2O_5$ 27%, CaO 38%, $SiO_2$ 15%, Cl 5%, F 2·2%) except that the optimum temperature is 1550°C. This also applies to a phosphorite ($P_2O_5$ 25%, CaO 40%, $H_2O$ 13%, $CO_2$ 4·5%, F 2·6%), but in addition fusion with lime and the mineral serpentine (39% MgO) and quenching were equally effective. In every instance an optical and *X*-ray examination showed that the quenched material was vitreous, whereas the slowly-cooled product was crystalline and had a fluorapatite structure.[222]

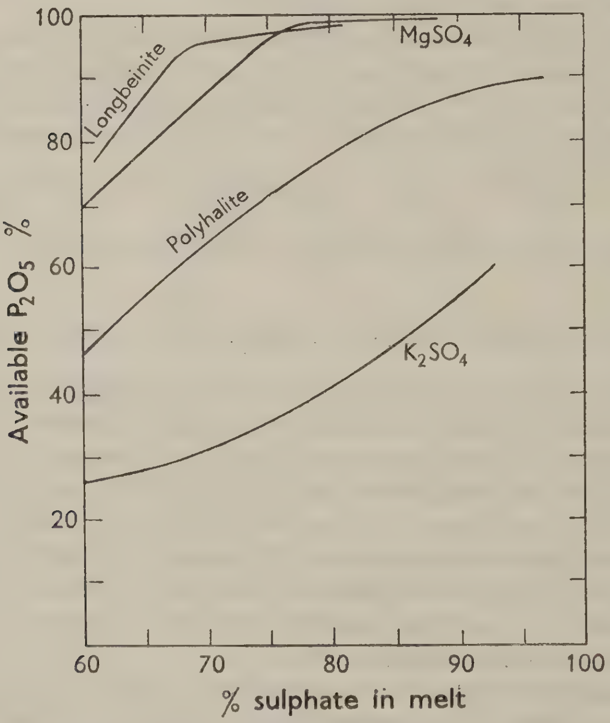

FIG. 13.—The reaction of Florida phosphate with sulphates at 1150°C.[216]

Mixtures of leucite, $KAl(SiO_3)_2$, and phosphate ore react with lime, dolomite, bauxite and calcium or sodium carbonates at temperatures above 750°C.[223]

Fusion of phosphate rock and a manganese silicate ore, followed by quenching from 1350°C. with a water-spray, is claimed to give a citrate-soluble product.[224]

A material which contains 70% of citrate-soluble $P_2O_5$ is said to result from calcining a mixture of phosphorite and monoammonium phosphate at 600°C.[225]

Phosphate rock reacts at 1000°C. with phosphoric acid and sodium chloride to give a material having good fertilizing properties.[226] A similar reaction occurs with aluminium phosphate ores at 800°C. in the presence of steam. The mechanism here seems to be the formation of sodium hydroxide from sodium chloride and steam at 700°C. or above, followed by reaction of the alkali to form complex sodium, calcium and aluminium phosphates.[227] Compounds of the type $CaNa_2(PO_4)_2$, $AlNa_6(PO_4)_3$ or $Na_3PO_4$ decompose phosphate rock at 1000°C.[228]

Phosphorus pentoxide in the vapour state reacts very readily with phosphate rock to form calcium metaphosphate. This fact has been used to produce high-grade phosphate fertilizers.[229] The large-scale manufacture of these from apatite has been described.[230] The process consists essentially in causing phosphorus pentoxide vapour to react with phosphate rock at 1100° (i.e. about 120°C. above the melting point of calcium metaphosphate) and then quenching to prevent crystallization. A product of low citrate-solubility and poor fertilizer value is obtained if the reaction is carried out below 1000°C. or the melt is not quenched.[231] Calcium metaphosphate does not absorb ammonia and must be hydrolyzed, e.g. with steam, if it is to be used for making ammoniated superphosphates.[232]

In a modification of the above process phosphorus is burned in air in the presence of water vapour and the combustion products are passed through phosphate rock at an optimum temperature of 1000°C. The main reaction is[233]:

$$3Ca_3(PO_4)_2,CaF_2+6P_2O_5+2HPO_3 = 10Ca(PO_3)_2+2HF$$

Potassium chloride may be used in the reaction to give a mixed calcium–potassium fertilizer. As a source of potassium the latter is somewhat better than potassium chloride for plant growth.[234] The composition and chemical and physical properties of calcium metaphosphate have been discussed in relation to its manufacture and use as a fertilizer.[235]

A study of the reaction of phosphorus pentoxide with Tennessee brown rock at 900°C. shows that in the initial stages the rate is governed by the transfer of phosphorus pentoxide through the gas surrounding the rock particles and is proportional to the $P_2O_5$ concentration in the gas phase. A coating of liquid products then begins to form on the particles and when this is complete the rate-determining factor is the transfer through the liquid layer. As the absorption of phosphorus pentoxide proceeds the absorption rate diminishes rapidly and there is no proportionality between this and the $P_2O_5$ concentration in the final stages of the reaction. At temperatures above 1000°C. resistance in the liquid phase becomes predominant only at high $P_2O_5$ concentrations. The absorption rate is very dependent on temperature and a temperature of at least 1000°C. in the absorption zone is required to maintain absorption rates high enough for production purposes.[236]

## Decomposition by Miscellaneous Methods

Many relatively simple methods have been proposed either for completely decomposing phosphorites or for improving their suitability for agricultural purposes.

About half of the phosphorus in phosphorites containing 12 to 30% $P_2O_5$ is said to become water-soluble on grinding with potassium sulphate and then extracting with hot water. Calcium carbonate retards this action and apatite gives only about 5% of soluble $P_2O_5$.[237]

Apatite and phosphorites are decomposed to the extent of about 70% when heated with sodium bisulphate solutions at an optimum temperature of 200°C. under pressure.[238] By a multi-stage treatment of apatite with sulphuric acid and sodium sulphate with recycle at each stage, a monosodium phosphate can be separated which is sufficiently pure for use in beverages.[311] Carbon dioxide solutions at about 50 atmospheres pressure react slightly with phosphorite to form calcium bicarbonate.[239]

Suspensions of ground phosphorite in water or dilute sulphuric or phosphoric acids are decomposed at 80° to 90°C. by treatment with air containing 3 to 5% each of nitric oxide and sulphur dioxide.[240] The amount of sulphur dioxide used should be equivalent to the phosphoric acid produced.[241]

Gaseous sulphur dioxide reacts only slowly with phosphate rock, even at high temperatures, but almost complete reaction occurs with aqueous solutions at pressures up to 3 atmospheres.[188] Finely-ground Florida rock is almost completely soluble in saturated aqueous solutions of sulphur dioxide under 3 to 10 atmospheres pressure and at temperatures of 25° to 100°C. The products of the reaction are elemental sulphur, calcium sulphate and sulphite and mono- and dicalcium phosphates.[242]

Phosphate rock reacts with aqueous solutions of lead chloride at room temperature according to the equation:

$$3Ca_3(PO_4)_2+10PbCl_2 = 3Pb_3(PO_4)_2,PbCl_2+9CaCl_2$$

If the product is dissolved in nitric acid so as to give a solution containing 145 g. $NO_3$ and 330 g. $P_2O_5$ per litre, most of the lead nitrate remains insoluble and can be filtered off and recovered as lead chloride by reaction with potassium chloride and ammonia.[243]

Phosphorites have been converted into soluble calcium and phosphorus compounds by an electrodialysis procedure.[244] Separation by high-voltage electrolysis is also possible.[245] In this method lime is precipitated at the cathode and phosphoric acid is concentrated in the anode compartment.[246]

### Decomposition of Aluminium Phosphates

Large deposits of aluminium phosphate ores occur in the Senegal region of North Africa and minerals such as wavellite, $Al_3(PO_4)_2,5H_2O$, crandallite, $CaAl_3(PO_4)_2,(OH)_5,H_2O$, and millisite, $(Na,K)CaAl_6(PO_4)_4(OH)_9,3H_2O$, are associated with the Florida phosphates. Chemical treatment of these phosphates is difficult, particularly with low-grade ores and on a commercial scale filtration and purification problems are involved. Some of the ores can be dissolved in sodium hydroxide to form trisodium phosphate and sodium aluminate. Some of the former can be crystallized if the sodium content of the solution is controlled so as to minimize the saturation with aluminate. The phosphorus may also be precipitated with lime and the aluminium then recovered.

It has been proposed to heat aluminium phosphate ores with carbon and sodium sulphate at 800°C. and then extract the trisodium phosphate with hot water.[247] If this process is carried out in the presence of steam, the extract contains trisodium phosphate, sodium aluminate and sodium hydroxide.[248]

In another procedure the phosphate is mixed with clay, carbon and siliceous material and is calcined in a rotary kiln. Phosphorus is recovered by condensing the vapour and the clinker is leached to give soluble calcium aluminate. The residue from this is treated to give an hydraulic cement.[249] Alternatively, a pelletized mixture of lime, alumina, carbon and defluorinated[312] phosphate rock can be heated at 1325–1425° in a rotary kiln. Most of the phosphorus is evolved[313–14] leaving a clinker suitable for Portland cement manufacture.[313]

An acid extraction has been used in which the ore is first calcined at 1000° to 1150°C. and is then treated with 42% nitric acid and 50% sulphuric acid, using 2·2 moles of each acid per mole of $P_2O_5$. About 90% of the $P_2O_5$ and 60% of the $Al_2O_3$ in the ore is extracted by this procedure.[250] Filtration rates are at a maximum and the amount of $Al_2O_3$ extracted is at a minimum (55%) when the calcining temperature is about 1000°C.[251]

## THE REMOVAL OF FLUORINE FROM PHOSPHATE ORES

Fluorapatite is a potential major source of fluorine. Although they are not at present exploited for their fluorine content, the quantity of phosphate ores used for commercial and industrial purposes is equivalent to a considerable tonnage of fluorine. It has been estimated[252] that the fluorine in the phosphate rock processed in the United States during 1958 was more than double that in the fluorspar which was mined in that year.

The fluorine/phosphorus ratio[253] and the fluorine content,[254] which may be as high as 5% or more but is usually about 3·5%, vary with the source of the phosphate. Typical analyses of different types of ore are given in Table III.[252–8]

The extraction of fluorine from phosphate ores does not compete economically with processes using high-grade fluorine minerals. On the other hand the removal of fluorine from phosphates is an important consideration in the utilization of the phosphorus. The use of phosphates as animal food supplements and as fertilizers requires a product having a low fluorine content.

In the conversion of phosphate rock to phosphoric acid by the wet-acid process as much as 30% of the fluorine in the rock may be present in the final acid.[83] Removal of the fluorine from the phosphoric acid is difficult, but can be achieved if the acid is converted into phosphates. Treatment with sodium carbonate to pH ~ 2 causes most of the fluorine to precipitate as sodium silicofluoride. The latter is least soluble at pH 5 and filtration of concentrated solutions at this stage gives monosodium phosphate which contains 0·1% or less of fluorine.[83]

*Table III.—Fluorine and Phosphorus Content of Some Phosphate Ores*[252–8]

| Source of phosphate | % F | % $P_2O_5$ |
|---|---|---|
| Florida hard rock | 3·4–4·0 | 31–36 |
| Florida land pebble | 3·2–4·1 | 30–36 |
| Florida soft rock | 0·2–3·8 | 15–35 |
| Tennessee brown rock | 2·6–4·1 | 25–38 |
| Tennessee blue rock | 3·3–4·0 | 28–34 |
| Tennessee white rock | 3·1–3·8 | 30–36 |
| Tennessee limestone | 1·0–2·3 | 10–19 |
| Montana, U.S.A. | 2·9–7·0 | 27–38 |
| Western States, U.S.A. | 3·1–3·8 | 26–35 |
| S. Carolina, U.S.A. | 2·2–3·8 | 16–29 |
| Curacao, West Indies | 0·3–0·9 | 38–41 |
| Algeria | 3·3–4·2 | 23–32 |
| Morocco | 4·1–4·3 | 33–35 |
| Tunisia | 3·5–3·8 | 26–29 |
| Egypt | ~3·5 | ~30 |
| Congo and Ruanda | 2·3–4·2 | 40–43 |
| Esthonia | 1·5–2·4 | 16–27 |
| Kola peninsula, U.S.S.R. | 3·2 | 39 |
| Nauru and Ocean Islands | 2·0–3·3 | 38–41 |
| Christmas Island | 1·0–1·5 | 39 |
| Pelew Islands | ~3·0 | ~40 |
| Vietnam | 3·0–3·5 | 38–40 |
| S. Australia | 3·3–3·6 | 30–34 |

Under certain conditions, a compound containing fluoride can precipitate with the gypsum during the initial attack of apatite by sulphuric acid. The compound has a unique *X*-ray pattern and forms regular octahedral crystals containing F, Ca, $SO_4$, Al, Si, and $H_2O$. Its formula is complex and has been variously reported as

$2{\cdot}5CaSO_4,3CaSiF_6,3CaAlF_5,2{\cdot}2CaF_2,25H_2O,$[315]
$4CaNa_mH_n(Al_xSi_{(1-x)})F_6,6CaF_2,3CaSO_4,44H_2O,$[316]
$Ca_3Al_2(R.E.)SO_4F_{13},12H_2O$[319] and
$CaSO_4,1{\cdot}5CaSiF_6,CaF_2,12H_2O$[317]

The addition of fluoride[315] or lime[318, 320] to the phosphoric acid will often assist its formation. Attention has been drawn to its isomorphism with the rare earth mineral chukhrovite, $Ca_3Al_2(R.E.)SO_4F_{13},10H_2O$.[319]

When phosphate rock reacts with sulphuric or phosphoric acids to give superphosphate most of the fluorine is transferred to the product. Under the best conditions only 10 to 40% of the fluorine is volatilized and the superphosphate generally contains 1·5 to 2·7%.[86] When it is mixed with lime or treated with ammonia, fluorapatite is formed with reversion of the phosphate to an unavailable form.[259] Several of the factors which influence the removal of fluorine in the superphosphate process have been studied using Florida pebble phosphate. The proportion of fluorine volatilized is increased by increasing the acid concentration, raising the acid/rock ratio, and by adding the concentrated acid to a mixture of the rock and water. Less fluorine is removed when mixtures of 70% sulphuric acid and 85% phosphoric acid are used than by either acid alone. The effect is shown in Fig. 14. With phosphoric acid alone there is a sharp increase in the volatilization of fluorine when the acid concentration is greater than 72% $H_3PO_4$.[260]

The action of sulphuric acid on phosphate rock may be considered to occur in two stages, in the first of which the main reaction is to form phosphoric acid which then reacts with undecomposed rock to give monocalcium phosphate. The mechanism of the volatilization of fluorine during these reactions has been variously interpreted. According to the early views calcium fluoride reacts with the sulphuric acid to form hydrogen fluoride. The latter then reacts with the silica in the rock to give silicon tetrafluoride, which is then partly hydrolyzed to fluosilicic acid. This is converted to hydrogen fluoride and silicon tetrafluoride by the action of heat in the presence of acid.[261] The reaction scheme is represented by the equations:

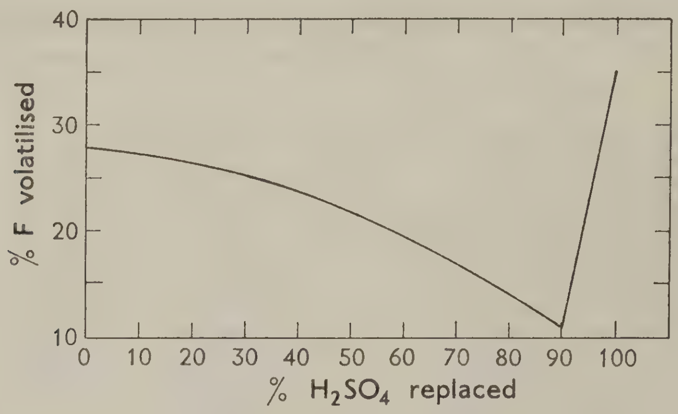

FIG. 14.—Effect of replacing sulphuric acid by phosphoric acid on the volatilization of fluorine from phosphate rock[260]

$$\begin{aligned} CaF_2+H_2SO_4 &= CaSO_4+2HF \\ 4HF+SiO_2 &= SiF_4+2H_2O \\ 3SiF_4+2H_2O &= SiO_2+2H_2SiF_6 \\ H_2SiF_6 &\rightleftharpoons SiF_4+2HF \end{aligned}$$

A later interpretation explains the mechanism by the equations[84]:

$$\begin{aligned} CaF_2+H_2SO_4+2H_2O &= CaSO_4{,}2H_2O+2HF \\ CaF_2+2H_3PO_4 &= Ca(H_2PO_4)_2+2HF \\ 6HF+SiO_2 &= H_2SiF_6+2H_2O \\ H_2SiF_6 &\rightleftharpoons SiF_4+2HF \end{aligned}$$

More recently[260] the above mechanisms have been questioned, mainly on the ground of the observation that on contact of phosphate rock with acid the major proportion of the fluorine is evolved as silicon tetrafluoride and not as hydrogen fluoride. There is also some evidence that hydrogen fluoride reacts more readily with phosphate rock than it does with silica. Fluorine evolution is increased much more by the addition of calcium fluosilicate to the reaction mixture[260] than by adding silica.[262] These facts are explained by assuming that the fluorine is present in phosphate rock as calcium fluosilicate.[263] Under anhydrous conditions, i.e. when sulphuric acid of concentration greater than 95% is used, the main reaction in the volatilization of fluorine is[264, 260]:

$$CaSiF_6+H_2SO_4 = CaSO_4+2HF+SiF_4$$

In the presence of water fluosilicic acid is formed:

$$CaSiF_6+H_2SO_4 = H_2SiF_6+CaSO_4$$

and its concentration in solution increases until it reaches the composition corresponding to the invariant complex $H_4SiF_8,12H_2O$.[265] This hydrate is formed by the reaction[260]:

$$2H_2SiF_6,6H_2O \rightleftharpoons H_4SiF_8,12H_2O + SiF_4$$

Various procedures have been devised for removing fluorine from superphosphate. Almost complete defluorination is achieved by heating the material for up to 30 min. at 700° to 900°C. The presence of water assists the reaction and also prevents reversion to fluorapatite.[266] Other calcination procedures[267] and the influence of various factors on the defluorination[268] have been reported. A large-scale manufacturing process based on these observations has been described in detail.[142]

Many investigations have also been made into the removal of fluorine from phosphate rock. Early observations indicated the importance of silica and of water in the defluorination process, but the necessity of having both present in the system was not clearly recognized. Consequently many of the methods proposed before about 1945 were not completely satisfactory when used on an industrial scale.

In one of the first systematic investigations of the problem it was found that 95 to 100% of the fluorine was removed by adding sand to the phosphate rock so as to make the total silica content about 45%. The mixture was then heated in an atmosphere of steam for up to 60 min. at 1400°C.[269] With closer control of the operation similar results were achieved with only 5 to 10% of silica in the mixture.[270] With ores such as Moroccan phosphate (which contains less than 1% $SiO_2$) only 50 to 60% of the fluorine is removed unless extra silica is added.[271–2] Vanadium and similar impurities are reported[252] to inhibit the defluorination of phosphate rock at 1450°C.

A product containing less than 0·1% F is obtained by mixing finely-ground phosphate rock with 45% of its weight of silica and then adding 40% of water to the mixture. The material is then calcined at 1350° to 1450°C. and quenched.[273] In a similar procedure more than 95% of the fluorine is removed by steaming a Kola apatite/silica mixture at 1450° to 1475°C. without chilling the product.[274]

The removal of fluorine by hydrothermal methods is said to take place in two stages. In the first of these isomorphous replacement of fluorine with hydroxyl ions occurs and this is followed by breakdown of the hydroxy-apatite into tri- and tetracalcium phosphates. Steam is necessary only in the first stage. Addition of silica, which reacts with the hydroxyapatite, results in the formation of a phase which has a variable composition and which is isomorphous with tricalcium phosphate.[275]

The addition of 2 to 3% of silica to phosphorites followed by steaming at 1370° to 1400°C. is reported to remove only 90% of the fluorine. The product is not soluble in 2% citric acid. Similar treatment of apatite completely removes the fluorine and gives a citrate-soluble product.[276]

One of the difficulties in operating the above procedures on a large scale is that it is not easy to control the temperature of the rock near its softening point. For this reason the defluorination of molten phosphate rock has been proposed. A detailed examination of this process in the temperature range of 1450° to 1600°C. shows that temperatures above 1500°C. have relatively little effect on the defluorination rate $R$. For shallow charges of molten rock the rate is given by

$$R = k\,\frac{w^{0\cdot 45}\,v^{0\cdot 30}}{d}$$

where $k$ is a constant and $d$, $w$, $v$ are respectively the charge depth, concentration of water vapour in the reaction atmosphere and the gas velocity over the charge. In deep charges the rate is governed by diffusion through the melt and $R$ increases with temperature and varies inversely with the square of the depth. Addition of iron and aluminium oxides and silica assists the defluorination. The theory of the process, velocity equations and graphical data have been given.[277]

Defluorination of phosphate rock on a commercial scale has been achieved by the melt-process, using either an arc electrode furnace[278] or an oil-fired furnace in which the water vapour is provided by the combustion products of the oil.[279] Products containing less than 0·1% F are obtained, but the furnace linings (refractory silica) are rapidly attacked by the melt.

### Recovery of Volatilized Fluorine

Various methods of absorbing and collecting the fluorine-containing gases evolved in defluorinating processes have been described.

Hydrogen fluoride can be absorbed in a tower containing limestone but the absorption slows down as the limestone becomes coated with calcium fluoride. A recovery of 87% has been achieved.[280] Partial pressures in the HF–$H_2O$ system,[281] and vapour pressure data for the HF–$H_2SiF_6$–$H_2O$[265] and HF–$H_2O$[282] systems have been reported. Hydrogen fluoride has been recovered from gases by absorbing it on solid sodium fluoride at 100°C. It is then recovered in a pure state by heating the solid at 275° to 350°C.[283–4] The equilibrium involved is[285]

$$HF + NaF \underset{>250°C.}{\overset{<200°C.}{\rightleftharpoons}} NaHF_2$$

Silicon tetrafluoride is absorbed as $Na_2SiF_6$ in this method, but is not decomposed when heated to 350°C.

The fluorine gases evolved from the treatment of phosphate rock with phosphoric acid containing 74% $P_2O_5$[152] contain 6% of the fluorine as hydrogen fluoride, the remainder being silicon tetrafluoride. These gases are absorbed by solutions containing ammonium fluosilicate and ammonium fluoride at pH 5·5 to 6. The solution is maintained at a constant pH by addition of an ammonia/ammonium fluoride solution having pH 8·5 to 9·0. The reactions involved are:

$$SiF_4 + 2NH_4F = (NH_4)_2SiF_6$$
$$2HF + NH_4OH = NH_4HF_2 + H_2O$$

Silica in an easily filtered form is then precipitated by neutralizing the solution to pH 8·5 to 9·0 with ammonia[286]:

$$(NH_4)_2SiF_6 + 4NH_3 + 2H_2O = 6NH_4F + SiO_2$$
$$NH_4HF_2 + NH_3 = 2NH_4F$$

The ammonium fluoride obtained from the above procedure can be converted into cryolite by reaction with an alkaline solution of sodium aluminate[283]:

$$6NH_4F + NaAlO_2 + 2NaOH = Na_3AlF_6 + 6NH_3 + 4H_2O$$

An alternative method is to use a solution of aluminium and sodium sulphates at pH 5·5:

$$12NH_4F + 3Na_2SO_4 + Al_2(SO_4)_3 = 2Na_3AlF_6 + 6(NH_4)_2SO_4$$

To avoid contamination of the cryolite with phosphate in these methods only 95% of the stoicheiometric amounts of sodium sulphate and aluminium compounds should be used. The F/$P_2O_5$ weight ratio in the solution must not be allowed to increase above 100.[283]

Ammonium hexafluoroaluminate can be precipitated at pH 5 to 7 from solutions containing ammonium fluoride and phosphate by addition of an aluminium salt. Heating the product at 500° to 550°C. causes the following decomposition:

$$(NH_4)_3AlF_6 = AlF_3 + NH_3 + NH_4HF_2 + NH_4F$$

The ammonia and ammonium fluorides are recycled in the process.[283]

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### SECTION III

# THE PREPARATION OF PHOSPHORUS

### BY D. R. PECK

## WHITE PHOSPHORUS

Most of the methods of preparing phosphorus have already been described (Mellor, VIII, 740), and an historical account has been given of the development of phosphorus manufacture.[272] With one or two exceptions much of the later work has been concerned with improving the earlier methods and applying them to commercial processes. These procedures, which usually involve the reduction of a phosphate by carbon in the presence of silica, require temperatures in the range of 1000° to 1500°C. if high yields of phosphorus are to be obtained. It has been found, however, that many phosphates can be reduced by hydrogen at temperatures between 300° and 750°C. Metals which do not form phosphides, or give phosphides which are easily dissociated by heat, are most susceptible to this reduction. In these reactions the metal is formed and the oxygen of the phosphate is quantitatively converted to water. Lead phosphates are particularly easy to reduce by hydrogen. For example, pyromorphite, $3Pb_3(PO_4)_2,PbCl_2$, starts to react at 300°C. and is completely reduced at 850°C.[1] The alkali metal and alkaline earth phosphates are not reduced under these conditions.

Phosphorus, however, can be prepared from tricalcium phosphate by first converting it into pyromorphite. The latter is formed by stirring the phosphate or a phosphorite in suspension in aqueous lead chloride at room temperature[2]:

$$3Ca_3(PO_4)_2 + 10PbCl_2 = 3Pb_3(PO_4)_2,PbCl_2 + 9CaCl_2$$

The pyromorphite is then reduced by hydrogen at 500° to 600°C.:

$$2[3Pb_3(PO_4)_2,PbCl_2] + 50H_2 = 20Pb + 3P_4 + 4HCl + 48H_2O$$

Phosphorus is also formed by reducing the ortho-, meta- or pyro-phosphates of tin, bismuth and lead in a stream of hydrogen at temperatures between 400° and 800°C.[3] The reduction of phosphates by hydrogen has been studied at temperatures up to 1000°C. and at pressures slightly above atmospheric. Water vapour formed in the reaction is continuously removed to prevent equilibrium being established. By plotting the pressure in the system against the temperature, the point at which each reaction becomes rapid can be determined. The results showed that the phosphates can be classified according to the type of reaction which occurs. Table I gives the decomposition temperatures for those phosphates which form phosphorus and the metal only.

Antimony phosphate forms a small quantity of antimony phosphide. Silver phosphate is reduced to silver and orthophosphoric acid at 140°C., and at 425°C. the acid is reduced to phosphorus. Between 300° and 350°C. the mercury phosphates form mercury and metaphosphoric acid which is reduced to phosphorus at 600°C. Stannic phosphate reacts slowly at 300° to 450°C., being reduced to stannous phosphate, which rapidly forms the metal and phosphorus at 600°C.

From a second group of phosphates metal phosphides are formed, usually

*Table I.—Decomposition Temperatures for Phosphates which are Reduced to the Metal and Phosphorus by Hydrogen*

| Phosphate | Decomposition temperature °C. |
|---|---|
| $BiPO_4$ | 425 |
| $Ag_3PO_4$ | 425 |
| $SbPO_4$ | 450 |
| $Pb_3(PO_4)_2$ | 575 |
| $3Pb_3(PO_4)_2,PbCl_2$ | 600 |
| $Hg_3PO_4$ | 600 |
| $Hg_3(PO_4)_2$ | 600 |
| $SnO_2,P_2O_5$* | 600 |

* Stannic phosphate of uncertain composition, containing some excess of $SnO_2$.

together with phosphorus. Decomposition temperatures and products for this group are given in Table II.

Cupric phosphates were reduced to metaphosphoric acid and cuprous metaphosphate at 300°C. On cooling from this temperature, cupric metaphosphate and metallic copper resulted:

$$2CuPO_3 = Cu(PO_3)_2 + Cu$$

The remainder of the phosphates studied gave various products. Phosphides were not major products and phosphorus was obtained only under certain conditions.

*Table II.—Decomposition Temperatures of Phosphates which give Phosphides, but no Metal, on Reduction by Hydrogen*

| Phosphate | Decomposition temperature °C. | Products |
|---|---|---|
| $Ni_3(PO_4)_2$ | 450 | $P+Ni_2P$ |
| $Ni_2P_2O_7$ | 550 | $P+Ni_2P$ |
| $Ni(PO_3)_2$ | 600 | $P+Ni_2P$ |
| $CuPO_3$ | 600 | $P+Cu_3P+CuP_2$ |
| $CrPO_4$ | 650 | $P+CrP+Cr_2P$ |
| $Co(PO_3)_2$ | 675 | $P+Co_2P$ |
| $Mn_3(PO_4)_2$ | 850 | $P+Mn_2P$ |
| $Fe_2P_2O_7$ | 600 | $FeP$ |
| $Co_3(PO_4)_2$ | 600 | $CoP+Co_2P$ |
| $Co_2P_2O_7$ | 600 | $CoP$ |
| $Zn_3(PO_4)_2$ | 600 | $Zn_3P_2$ |

Table III summarizes the data.[4] The reduction by hydrogen at 1000° of a crude aluminium phosphate from Senegal, predominantly crandallite and millisite, yielded 59% of the phosphorus. The residue contained alumina, $\beta$-tricalcium phosphate and ferrophosphorus.[263]

Many of the earlier reactions (Mellor, VIII, 740–3) in which phosphorus is formed have been applied to commercial processes in which the object is the maximum utilization of phosphate ores. In these procedures phosphorus manufacture is combined with that of by-products of industrial value. Such processes have been devised for phosphate ores which are not generally suitable for the electrothermal production of phosphorus.

In some of the methods the main by-product is an aluminous cement or similar material. Naturally-occurring aluminium phosphates may be mixed with lime, silica and charcoal and smelted to give a calcium aluminate cement, and the phosphorus recovered as phosphoric acid.[5] Mixtures of calcium and aluminium phosphates[6] or of calcium phosphate and aluminous materials[7] can be used, and the process may be used for the simultaneous production of yellow phosphorus and aluminous cement.[264–5] Addition of bauxite[8] and the use of bauxite instead of silica[9] have been proposed. If relatively pure phosphate is available the slag may be used as a raw material for the manufacture of aluminium.[10] A hydraulic cement is obtained if the proportions of the reactants are chosen so as to produce a slag with a composition in the range: $Al_2O_3$ 12–35%, CaO 40–55% and $SiO_2$ 18–38%.[11] Phosphorus and cements may also be obtained by smelting phosphates with carbon and potash minerals such as feldspar or leucite in the presence of alumina,[12] or by using bauxite containing iron.[13] Fluorine in the phosphate is eliminated by adding alkali metals and melting in the presence of water vapour.[14]

*Table III.—Reduction by Hydrogen of Phosphates which do not form Phosphides as Major Products*

| Phosphate | Decomposition temperature °C. | Products |
|---|---|---|
| $Cu_3(PO_4)_2$ | 300 | $CuPO_3+HPO_3$ |
| $Cu_3(PO_4)_2$ | 600 | $CuPO_3+$ some $Cu_3P$ |
| $Cu_2P_2O_7$ | 300 | $CuPO_3+HPO_3$ |
| $FePO_4$ | 460 | $Fe_2P_2O_7$ |
| $(UO_2)_3(PO_4)_2$ | 550 | $3UO_2,P_2O_5$ |
| $(UO_2)_3(PO_4)_2$ | 750 | $P+UO_2$ |
| $H_3PO_4+SiO_2$ | 550 | P |

It has been proposed to manufacture phosphorus and pure alumina by heating aluminium phosphate minerals with carbon at temperatures above the melting point of alumina.[15] In a variation of this process iron sulphides,[16] or iron and sulphur compounds,[17] are melted with carbon and aluminium phosphate. If silica is also added, phosphorus and aluminium–silicon alloys are obtained.[18]

Phosphorus and lithium compounds can be obtained from lithium-containing phosphorites, e.g. amblygonite and triphyllite, by heating them with silicon. Phosphorus is volatilized and lithium silicates remain.[19]

Smelting of phosphorite and potassium silicate minerals with carbon in an electric furnace,[20] or in a blast furnace,[21] volatilizes both the phosphorus and potassium. Phosphorus and potassium hydroxide can be recovered by heating a mixture of charcoal, phosphorite and a potassium aluminium silicate such as feldspar.[22] Chlorination of phosphate rock with excess of chlorine in the presence of carbon yields the trichlorides of phosphorus, aluminium and iron as gaseous products. If the gases are then passed over a heated mixture of carbon and orthoclase, phosphorus and potassium chloride are also formed.[23]

The combined manufacture of phosphorus and calcium compounds has been suggested in a number of processes. In one of these Moroccan phosphate, kaolin and coal are heated to 1600°C. and phosphorus, alumina and calcium oxide are recovered.[24] A slag which readily disintegrates and is easily soluble in acid is obtained from this procedure by adjusting the proportions of the reactants so as to form a product containing 45–60% CaO, 10–30% $SiO_2$ and 10–40% of iron and aluminium oxides.[25] Reduction of tricalcium phosphate, phosphorite or other tertiary calcium phosphate with charcoal at 1600° to 1750°C. in an atmosphere of carbon monoxide volatilizes the phosphorus, leaving a mixture of calcium oxide and charcoal. Further heating in the presence of carbon monoxide forms calcium carbide.[26] The procedure may be carried out in a kiln-type electric furnace.[27] The calcium carbide obtained in this way often contains traces of phosphorus which are eliminated by heating at 900°C. in a stream of nitrogen to convert the carbide into calcium cyanamide.[28] Simultaneous production of the latter and of phosphorus is achieved by heating phosphorites and coal, anthracite or peat at 1000° to 1600°C. in the absence of silica, the last traces of phosphorus being removed by heating to 1600–1900°C. The residue is then heated in nitrogen at 1000–1200°C.[29] Phosphorite and calcium carbide in the presence of a little calcium fluoride are said to form phosphorus and cyanamide at 1000°C. in a nitrogen atmosphere.[30]

Active carbon and phosphorus have been made from phosphoric acid by kneading the latter with organic material, e.g. sawdust or peat, and carbonizing at 300°C. The residue is then heated for 8–9 hr. at 900° to 1200°C.[31] Monocalcium phosphate may be used in this procedure instead of phosphoric acid.[32] Phosphine and carbon monoxide are also products of this reaction.[33]

Hydrogen is obtained as a by-product of the reduction of phosphates to phosphorus, by heating the phosphate with silica at 1200° to 1300°C. in an atmosphere of methane,[34] or by blowing hydrocarbons into the melt.[35] The reaction occurs at 1000°C. in the presence of silicates, when carbon monoxide is also formed.[36]

At electric furnace temperatures silicon replaces the phosphorus in ferrophosphorus.[37] Ferrosilicon or mixtures which produce silicon at high temperatures may be used in this reaction.[38] A similar method using sulphur has been proposed.[39] Carbon and silica behave in a similar way.[40] An alternative procedure is to cause the ferrophosphorus to react at 500° to 700°C. with insufficient chlorine to chlorinate it completely. This yields phosphorus and ferrous chloride which is recovered by decantation from the residue at 700–1250°C.[41]

Mixtures of crude phosphate, chromium ore, coke and silica yield phosphorus in the electric furnace, together with a chromium–iron–phosphorus alloy. Heating the latter with sodium hydroxide in the presence of oxygen converts it into dichromate.[42]

In one of the more direct procedures for preparing phosphorus, phosphate is heated with carbon and silica at 1400°C. in the presence of a molten chloride such as sodium chloride.[43] Another method uses 100 parts of tricalcium phosphate, 100 parts of aluminium phosphate and 48 parts of charcoal. At 1500–1600°C. the reaction is[44]:

$$2AlPO_4 + Ca_3(PO_4)_2 + 10C = Al_2O_3 + 3CaO + P_4 + 10CO$$

Lower reduction temperatures (about 1200°C.) are said to be required if the source of carbon is pitch, asphalt or a similar material which is absorbed by the phosphate.[45] Tricalcium phosphate is reduced to phosphorus when heated with coke, heavy metal sulphides, e.g. those of iron, lead, copper or zinc, and an easily fusible sulphide such as potassium, magnesium or aluminium sulphide. The temperature is kept high enough to decompose the heavy metal sulphide, but below the dissociation point of calcium sulphide.[46]

### Production of Phosphorus by Blast Furnace and Similar Methods

As an alternative to the electrothermal process for the manufacture of phosphorus, many procedures have been examined in which blast or shaft furnaces or similar types of equipment have been used. Most of these were designed for phosphorus ores such as apatite or tricalcium phosphate, or for phosphorites containing mainly calcium phosphates. They can, however, be used with ores having a lower phosphorus content than that normally required for the satisfactory operation of the electrothermal process.

Although the method of operating these furnaces varies with the type of equipment used and is also dependent on the composition of the phosphate ore, the basic procedure is to mix the ore with carbon and silica in some suitable form and then heat to a high temperature.

The very early processes for the manufacture of phosphorus by furnace or retort procedures were essentially commercial developments of the methods previously described (Mellor, VIII, 740–1). The possibility of reducing tricalcium phosphate by carbon and silica in a furnace at high temperature was first demonstrated by Berthier in 1826.[47] He observed that the ease of reduction increased with the proportion of silica used, that calcium phosphide was not formed, but that any iron phosphate present formed only iron phosphide. Three years later Wöhler repeated this and obtained phosphorus and carbon monoxide by heating in a retort a mixture of calcined bone with half its weight of sand and a little lampblack.[48] Schloesing showed that all the phosphorus could not be extracted by heating calcium, magnesium or aluminium phosphates with carbon only, because of poor contact between the reactants.[49] Addition of silica gave complete reduction because a melt was obtained.[50–1] Brisson[52] in 1868 was the first to propose the large scale manufacture using mineral phosphate, coke and a flux in a blast furnace operation. A vertical furnace has been suggested.[53] Readman examined the problems of the blast furnace procedure in an experimental manner.[54]

The operation of a blast furnace process on a commercial scale has been described.[55] Phosphate rock was briquetted with half of the amount of carbon required to reduce it to phosphorus, a larger proportion causing serious blocking of the furnace by the slag formed. The furnace was charged with the briquets, silica and coke in proportions to give a slag having a $CaO:SiO_2$ weight ratio of 1·2. The phosphorus could be burned to phosphorus pentoxide and then hydrated to phosphoric acid. However, a purer acid was obtained by separating the phosphorus and burning and hydrating it in a further stage. In order to improve the thermal efficiency of the process it was necessary to burn part of the exit gases in heat exchangers and use the heat to pre-heat the air blast. The remainder of the gas was used for steam raising. From calculations of the heat balance of a small experimental blast furnace it has been estimated that the thermal efficiency of the reduction is 5–10%.[56]

Various ways of utilizing the exhaust gases from the blast furnace have been studied. The carbon monoxide present may be oxidized, caused to react with steam and the resulting gases used for ammonia or methanol synthesis.[57] The phosphorus in the gas can be recovered by oxidation to phosphoric acid with steam and air and then passed over lime at 600–750°C. Alternatively the phosphorus can be oxidized to phosphorus pentoxide so as to recover the heat of combustion, with simultaneous formation of superphosphate.[58] The rate of oxidation of the phosphorus-containing gases in the presence of air, steam and lime at 550–950°C. has been found to be very high, even at high velocities of the gas stream. Sodium chloride may be used instead of lime so as to recover the phosphorus as sodium phosphates. Under these conditions the temperature must be limited to 400–500°C. to prevent volatilization of salt.[59] It has been proposed to oxidize the phosphorus and phosphine in the gases by scrubbing with nitric acid. The oxidation of the phosphine is largely due to the oxygen in the air, but nitric acid catalyzes the reaction.[60]

Methods of operating[61] a blast furnace, and the preparation,[62] size,[63] and physical form[64] of the charge have been described. Retaining the slag in the furnace for 2–4 hr. and operating at 1450°C. with an oxygenated air blast containing 30–45 wt.-% of oxygen is said to improve the volatilization of phosphorus.[65] The amount of carbon used in the reaction appears to be decreased by dehydrating the incoming air.[66] Improved efficiency of operation is claimed to result from maintaining the reaction zone in the furnace at above 1400°C., keeping the temperature of the exit gases below 400°C. and heating the air blast to at least 700°C.[67] The use of aluminium silicate as flux[68] and of silicon or silicon–iron alloys[69] has been suggested. Other variations,[70] modifications in furnace design,[71] and alternative methods of charging the furnace,[72] have been proposed.

Shaft furnaces have been used as an alternative to the blast furnace. In one of the earliest of these the shaft acted as a melting zone for a mixture of phosphate rock, sand and coke. The melt was then transferred to a slag chamber where phosphorus was volatilized, and withdrawn via the shaft.[73] Similar processes have been described in which the charge is fritted,[74] or sintered,[75] rather than melted. Variations of the procedure have been proposed.[76] A furnace having two reaction chambers has been used in an attempt to improve the thermal efficiency of the process.[77] Most of these procedures do not seem to offer any advantage over the blast furnace process.

More recently fluidized beds have been applied to phosphorus production. In one case finely ground phosphate rock was fluidized with hydrocarbon, and carbon cracked on to it at 950–1000°C. The coated rock was heated with silica for 1–8 hours at 1000–1300°C. in a second fluidized bed, when it evolved most of its phosphorus.[278] A similar procedure has been adopted for phosphate–shale mixtures,[279] and the electrical resistive heating of fluidized carbon-coated particles of phosphate has been proposed.[280]

### FACTORS WHICH AFFECT PHOSPHORUS YIELDS

Investigations carried out with shaft or blast furnaces have yielded information on the reactions occurring during the high temperature reduction of phosphate ores. Thus both carbon and silica were shown to be necessary for high extraction of the phosphorus from fluorapatite ore heated in a shaft furnace. The effects of time and temperature on the extraction are shown in Table IV for two mixtures.

*Table IV.—Volatilization of Phosphorus from Phosphate Rock*

| 50% rock + 50% carbon | | | 63% rock + 21% carbon + 16% sand | | |
|---|---|---|---|---|---|
| Time min. | Temp. °C. | Extraction % | Time min. | Temp. °C. | Extraction % |
| 78 | 1300 | 61 | 75 | 1400 | 73 |
| 78 | 1300 | 42 | 75 | 1450 | 91 |
| 85 | 1400 | 27 | 75 | 1500 | 94 |
| 80 | 1450 | 40 | 15 | 1550 | 78 |
| 96 | 1500 | 38 | 75 | 1550 | 96 |
| 15 | 1550 | 37 | 90 | 1550 | 98 |
| 85 | 1550 | 53 | | | |
| 105 | 1550 | 70 | | | |
| 85 | 1600 | 67 | | | |
| 120 | 1650 | 92 | | | |

The effect of varying the lime: silica ratio was determined by heating at 1500°C. for 45 min. mixtures which contained a 50% excess of carbon over that required for the reaction:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 2P + 5CO$$

The results, shown in Table V, indicate that high ratios decrease the amount of phosphorus extracted.

*Table V.—Effect of Lime: Silica Ratio on the Volatilization of Phosphorus from Phosphate Rock and 50% Excess of Carbon*

| $CaO:SiO_2$ wt. ratio | Phosphorus extracted % |
|---|---|
| 2:3 | 96·8 |
| 1:1 | 98·4 |
| 3:2 | 96·5 |
| 2:1 | 85·0 |
| 3:1 | 68·0 |

For mixtures ground to a fineness of 200 mesh or smaller it was observed that in the absence of carbon melts were obtained at 1300° to 1400°C. Addition of carbon raised the melting temperature and with sufficient present the temperature could be raised to 1650°C. without fusion occurring.[78]

A detailed study of the behaviour of an experimental blast furnace using an enriched blast (41% $O_2$ or 2·2 lb. of oxygen per lb. of $P_2O_5$ in the mixture charged to the furnace) showed that it is necessary to maintain strongly reducing conditions in the shaft of the furnace. For successful operation of the furnace it is essential to adjust the proportions of the ingredients in the charge to give a slag which is very fluid in the molten state. The best temperature for removal of the slag is 1500°C. Use of pure oxygen in the blast causes excessive volatilization of silica, but if the oxygen content in the inlet air is less than 40%, coke consumption is increased and the amount of phosphorus extracted decreased.[79]

The amount of phosphorus which can be extracted from phosphorites at a given temperature in the presence of carbon and alkali metal is greatest when the mixture contains, per mole of phosphorite, 3 moles of silica, 0·5 mole of aluminium oxide and 1 mole of sodium sulphate. Lower yields occur if the sodium sulphate is replaced by sodium carbonate or chloride.[80–1]

Sublimation of phosphorus from a mixture of fluorapatite and wood charcoal, without added silica, is complete in 1 hr. at 1600°C. No calcium phosphide was observed at this temperature but considerable quantities were formed at 1700° to 1800°C. At 1250° to 1450°C. only insignificant volatilization of fluorine occurred, but this increased when silica was added. For a silica : lime ratio of 1·07 about 52% of the fluorine was evolved in 1 hr. at 1450°C.[82]

Measurements of the rate of reduction of phosphorus ores by carbon at 1300°C. have shown significant differences in the behaviour of tricalcium phosphate, hydroxy-apatite and fluorapatite.[83]

Some observations have been reported on the operation of a blast furnace in a process designed for the production of phosphoric acid. Coke containing 87% of carbon was used and the consumption of this was measured in terms of the weight of coke per unit of phosphorus pentoxide reduced to phosphorus. The coke consumed was not affected by varying the air blast between 334 and 466 cu. ft. per minute. The furnace temperature was related to the coke consumption in a linear manner, as shown in Table VI.

*Table VI.—Effect of Furnace Temperature on the Coke Consumed in a Phosphorus Blast Furnace*

| Temp. °C. | lb. coke used per lb. $P_2O_5$ in charge |
|---|---|
| 650 | 4·5 |
| 805 | 3·7 |
| 865 | 3·5 |
| 940 | 3·2 |
| 965 | 3·1 |
| 1000 | 3·0 |

A reduction in coke usage was also found when the particle size was ½ in. or less, and the furnace was easier to operate when the phosphate rock feed contained not more than 20% of material smaller in size than 10 mesh. Thermochemical and heat balance calculations indicated that the thermal efficiency could vary between 38 and 75%. This depended on the heat insulation of the furnace, the type of filling and the method of operation.[84]

In place of coke, it has also been proposed to use methane as a reducing agent.[256] In the presence of silica, sodium sulphate and magnesium sulphate, 99% of the phosphorus in a phosphorite ore was recovered in 5 minutes at 1400° using a methane oxygen mixture.[256] At temperatures greater than 1300° the reduction is primarily by hydrogen.[257–9] The process has not found application commercially.[258–60]

The production of phosphorus by the blast furnace and similar procedures has not attained the industrial prominence of the electrothermal process. Apart from being less competitive as regards the purity of the end products, there are difficulties in preparing the furnace charge, in the construction of equipment and in the collection of the products, particularly the recovery of phosphorus from the outlet gases. Fuel economies and the recovery and distribution of waste heat in the process are generally less favourable than in the electrothermal procedure. The relative merits of the two methods have been discussed[85] and assessed.[86–7] The use of a nuclear reactor for phosphorus manufacture has also been suggested.[282]

### Production of Phosphorus by the Electrothermal Process

The use of electrical energy for the production of phosphorus on a commercial scale was first achieved by Readman, who obtained a patent for the process in 1888. A similar procedure was independently patented later in the same year by Parker and Robinson.[88] The earlier history of the industrial development of the electrothermal method has been variously described by Van Wazer[85] and others.[86, 89–91, 272] Descriptions have also been given of the equipment, and methods of operating in England,[92] America,[93] France,[94] Germany[95] and the U.S.S.R.[96]

The electrothermal method of preparing phosphorus differs from many other industrial electrical processes in that only the thermal effect of the electric current is used. Electrolytic effects, such as occur in the production of magnesium or aluminium for example, are not involved. In a phosphorus furnace the current passes through the charge and heat is developed partly by arc and partly by resistance phenomena. The operation of the furnace is essentially a reduction process and this distinguishes it from the resistance, induction or direct-arc furnaces commonly used in the melting and refining of metals.

Many investigations have been made into the design,[97–103] operation[104–11] and performance[112–14] of phosphorus furnaces. Experience has shown that it is easier to supply the large amount of electric power required by using alternating rather than direct current. This also makes it easier to control the current and voltage. In single-phase furnaces a greater concentration of heat under the electrode can be achieved if, instead of using two electrodes, only one is used and the bottom of the furnace or crucible serves for the other connection. However, single-phase operation has the disadvantage of unbalancing the power supply and a three-phase furnace is to be preferred. Two arrangements of the latter are possible. Three electrodes can be mounted in a line, giving a rectangular furnace which is fairly easy to construct. On the other hand this arrangement makes it difficult to maintain an electrical balance between the three electrodes. This can be avoided by fixing them at the corners of a triangle and constructing a cylindrical furnace.

The electrodes are cylinders up to 40 inches in diameter and may be made of graphite or baked carbon. The Soderberg electrode, made by packing a paste of coke and tar into a steel cylinder, has been proposed. This bakes into a rigid electrode under the heat developed in the furnace and can be replaced at the top so as to give continuous operation as the lower part is worn away. In phosphorus furnaces, however, the Soderberg electrode is not widely used, partly because of mechanical difficulties involved in adapting the system to enclosed furnaces. In addition the low consumption of carbon or graphite electrodes usually does not justify the extra cost of installing the Soderberg electrodes.[115]

The furnace consists of a mild-steel casing which can be water-cooled if necessary. It has a lining of firebrick, within which is another lining of carbon bricks up to the level of the molten slag. Two tap-holes are usually provided, one near the bottom of the furnace for removing ferrophosphorus and the other just above it for discharging the silicate slag. The roof of the furnace is lined with firebrick or similar material and is provided with a gas take-off, electrode holders, cleaning and poke holes, and closed chutes for feeding in the raw materials. The equipment is made air-tight and is operated under a slight positive pressure. The operation of furnaces at internal pressures of up to 50 kg./cm.$^2$ has been claimed[281] to give shorter reaction times and smoother operation, but no commercial use of this is known in phosphorus manufacture.

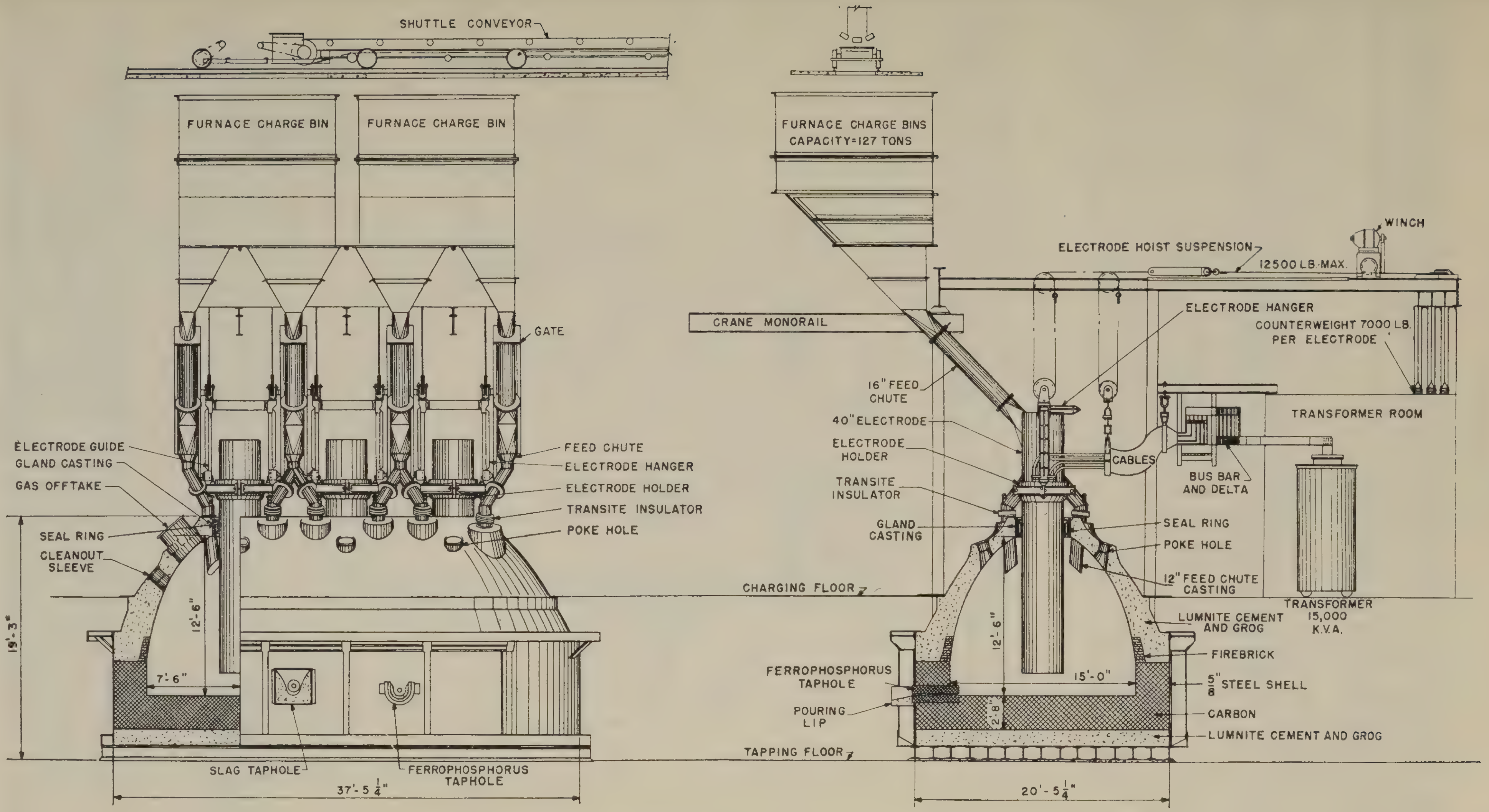

FIG. 1.—General arrangement of T.V.A. No. 6 phosphorus furnace

The current used by a three-phase furnace depends on its size and varies between 5000 and 50,000 amps. The potential difference between the electrodes is usually between 170 and 300 volts. The largest furnace in operation in 1960 had an electrical energy consumption of 50,000 kilowatts.[85]

### A RECTANGULAR FURNACE

A furnace operated by the Tennessee Valley Authority[116] is shown in Fig. 1.

This is a rectangular-type furnace of 13,400 kilowatts capacity with three in-line electrodes operating at a potential of 300 volts. Under normal conditions 14 lb. of electrode are consumed per ton of $P_2O_5$ in the furnace charge and 97% of the $P_2O_5$ is reduced to phosphorus. 87% of the phosphorus in the charge is recovered as the element. The electricity consumption is 6·1 kwh. per lb. of phosphorus recovered. This figure depends on the size of the furnace and on the quality of the raw materials used. Other values of 6·5–7[85] and 5·8–7[86] kwh. per lb. of phosphorus have been given.

### A ROTATING FURNACE

A rotating furnace, originally designed for producing calcium carbide and iron alloys[117] has been adapted for producing phosphorus.[118] This is shown diagrammatically in Fig. 2. The furnace is of cylindrical type, 3-phase, with a triangular

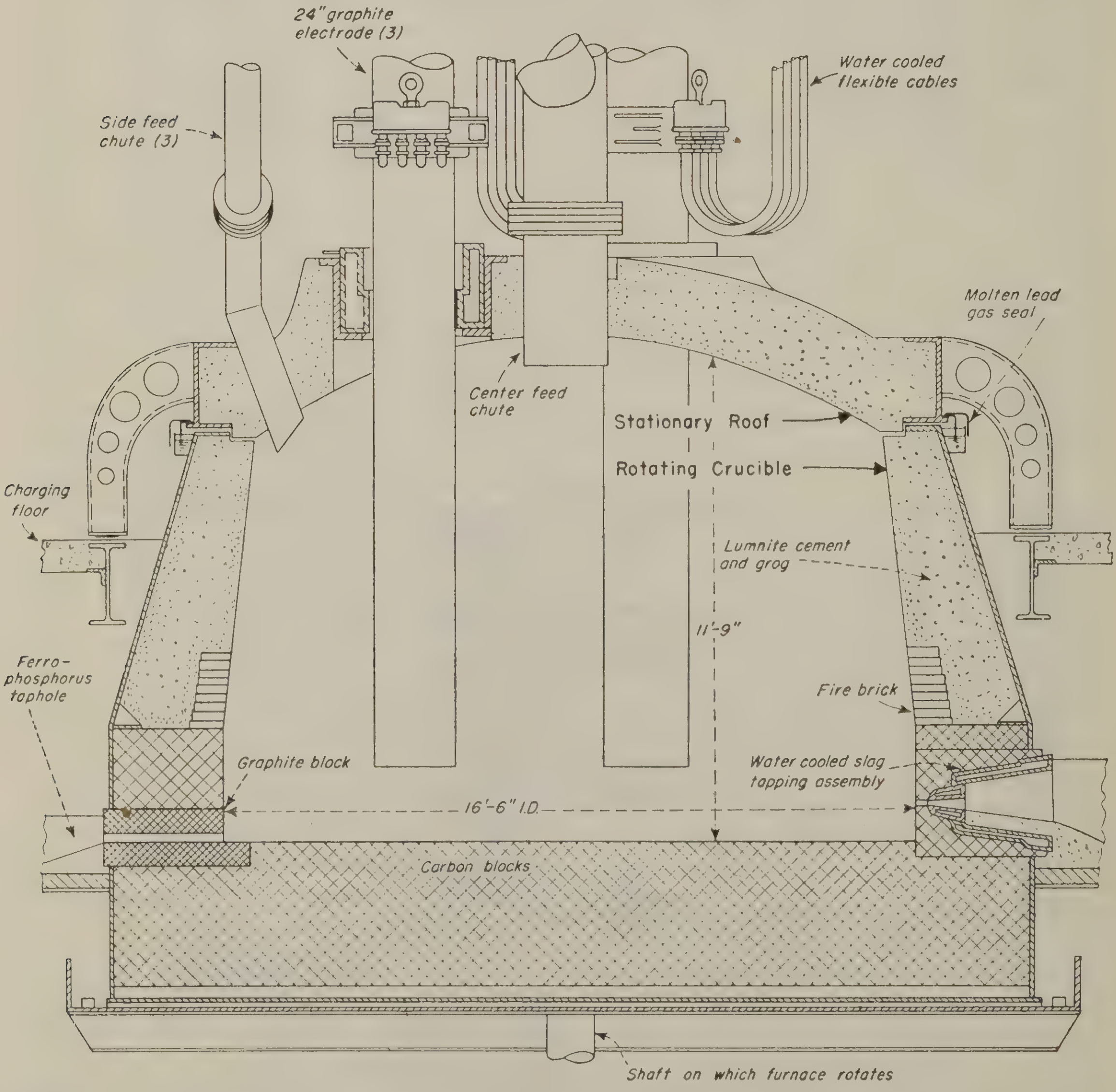

FIG. 2.—A rotating phosphorus furnace with stationary roof, electrodes, cables and feed chutes

arrangement of electrodes operating at a phase voltage of 300–350 volts. The capacity is 7500 kilowatts. The electrodes are stationary and the bottom of the furnace can be rotated at a speed of between 20 and 100 hr. per revolution. Consumption of electrodes varies between 7 and 12 lb. per ton of $P_2O_5$ in the charge. For short periods of operation the electricity consumption is 5·5 kwh. per lb. of phosphorus produced. This decreases to 5·1 for continuous operation.[119] Other advantages of the rotating furnace are increased life of the lining and the use of cheaper phosphate fines instead of lump material. A similar furnace of 25,000 kw. capacity has been described,[269] as has the design and operation of a plant based on the rotating furnace.[270]

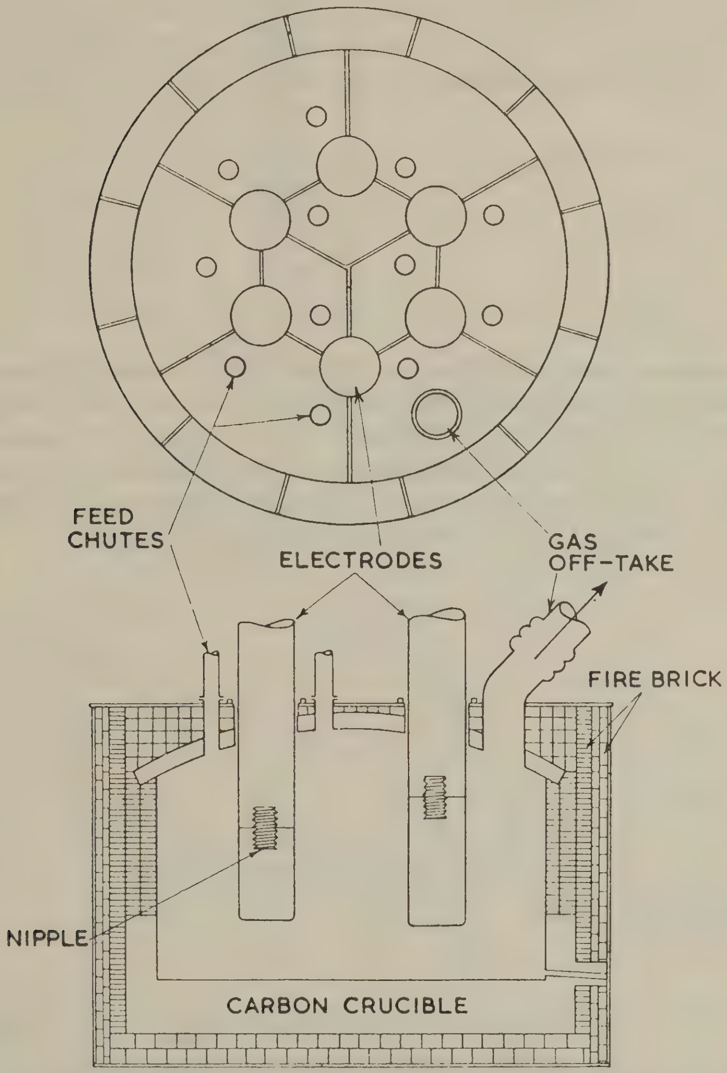

FIG. 3.—Diagrammatic sketch of a circular six-phase electric furnace

A six-phase furnace of cylindrical construction has been described[120] and is shown in Fig. 3. Observations[121] and data[122] on other furnaces have been reported. The principles to be followed in the design and construction of high efficiency phosphorus furnaces have been discussed in terms of the nature of the feed, furnace dimensions and other parameters.[271]

### THE CHARGE

In the operation of an electric furnace a phosphate ore with a minimum $P_2O_5$ content of 25% is generally required.[123] The charge must be maintained in a sufficiently porous state to allow the gaseous products to escape freely. The most suitable size for the raw materials is 0·5 to 2 in. If the phosphate rock has a small particle size, it must be agglomerated in some way. This may be done by briquetting,[124] nodulizing,[125] sintering with coal or by pellet formation in some suitable way.[126] Poor quality rock, especially if high in calcium carbonate, can be improved for electric furnace use by a preliminary heat treatment at 950–1050°.[261]

*Table VII.—Reduction of Fluorapatite by Various Forms of Carbon*

| Reducing agent | Temp. °C. | % $P_2O_5$ reduced |
|---|---|---|
| Lampblack | 1400 | 26 |
| | 1450 | 45 |
| | 1500 | 62 |
| Metallurgical coke | 1400 | 55 |
| | 1450 | 65 |
| | 1500 | 70 |
| Petroleum coke | 1400 | 31 |
| | 1450 | 49 |
| | 1500 | — |
| Pitch | 1450 | 76 |
| | 1500 | 90 |

The carbon used is generally in the form of coke or anthracite. Some differences in the relative reducing efficiencies of various forms of carbon have been noted,[127] but this effect seems to be dependent on the reaction temperature.[128] Some data are given in Table VII for the reduction of fluorapatite with the theoretical amount of carbon to reduce all the $P_2O_5$, in the presence of sufficient silica to give a $SiO_2:CaO$ weight ratio of 0·85 in the mixture,[116] the reaction time being 10 min.

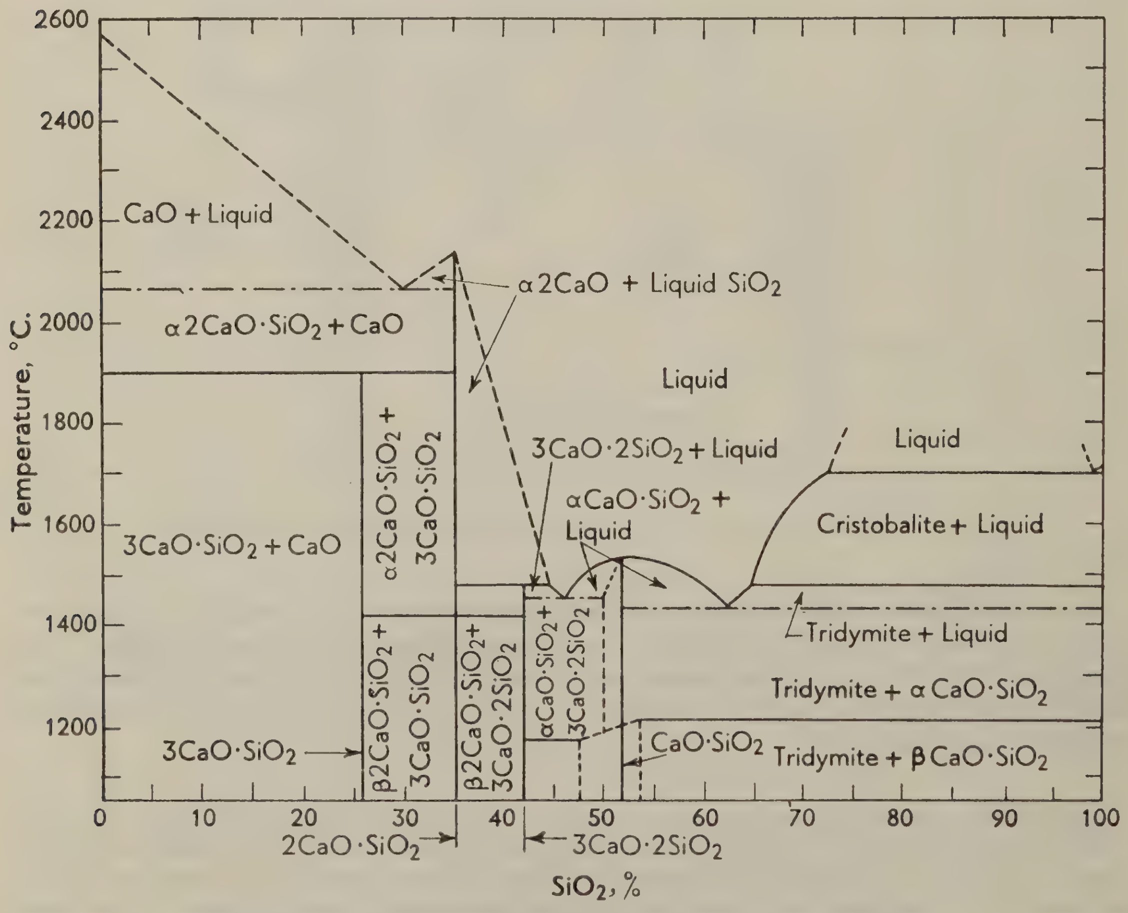

FIG. 4.—Equilibrium diagram for the system CaO–SiO₂

The composition of the charge has an important bearing on the operation of a phosphorus furnace. The properties of the slag and the amount of it produced are determined by the lime:silica ratio. Experimental furnaces have been operated with $CaO:SiO_2$ weight ratios varying between 0·70 and 2·00 (reference 116, p. 245), but for commercial production it is considered that for smooth operation of the furnace the ratio should be unity[86] or between 1·1 and 1·25.[129] With ratios of 0·6–0·9, more easily fusible slags are obtained and the yield of phosphorus increases somewhat, but more electrical energy is required and the attack on furnace linings is increased. With more basic compositions, i.e. $CaO:SiO_2$ ratios between 1·30 and 2·0, increasing quantities of silica are volatilized with the phosphorus. This appears to be a consequence of an increase in the fusion temperature of the charge. Any silica coming in contact with a melt at high temperature tends to be volatilized before slag formation occurs.[130] The $CaO–SiO_2$ equilibrium diagram[131] is shown in Fig. 4.

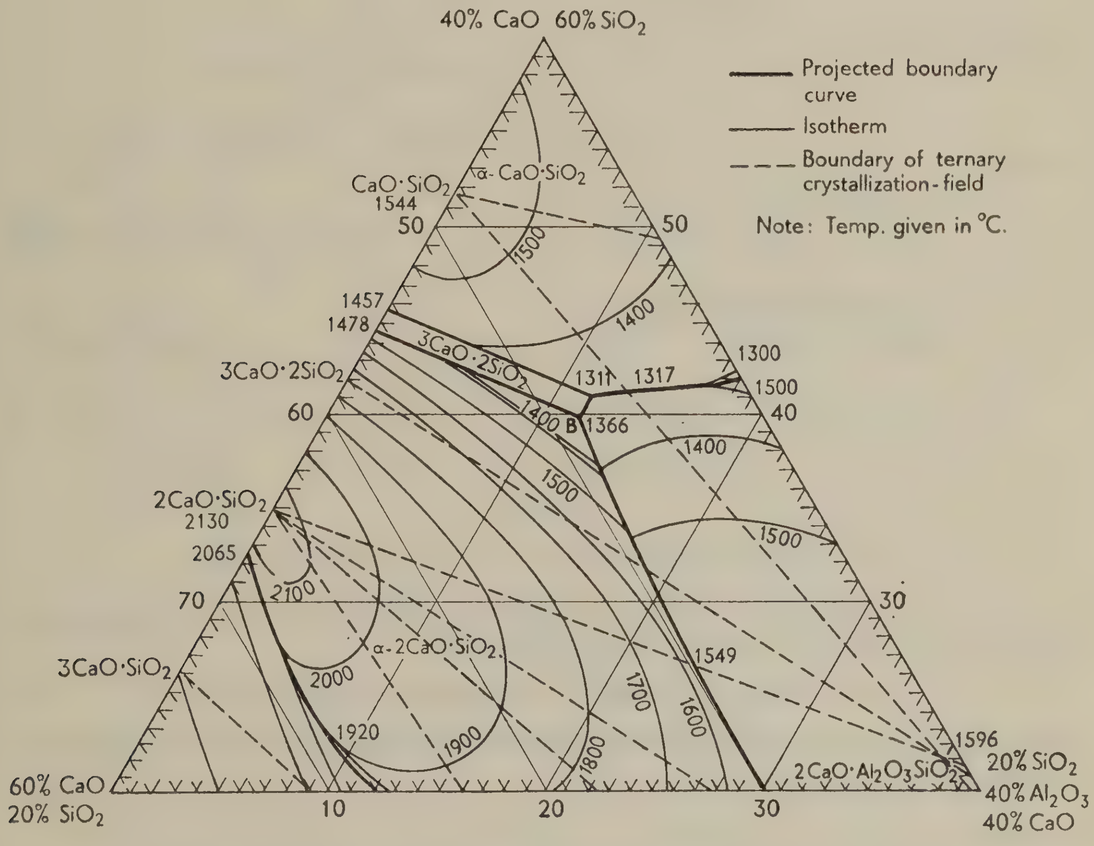

FIG. 5.—Equilibrium diagram for the system $CaO–Al_2O_3–SiO_2$

Any alumina which is present in the charge enters the slag and forms compounds with the lime and silica in the latter. An alumina content of up to 10% in the slag lowers the fusion temperature and causes difficulty in operating the furnace. On the other hand alumina acts as a fluxing agent and can be used to replace part of the silica in the charge. Experimental observations are reported.[116] Phase diagrams of the $CaO–Al_2O_3–SiO_2$ and $CaO–Al_2O_3$ systems[132] are shown in Figs. 5 and 6. The $Ca_3(PO_4)_2–SiO_2$ system has also been investigated.[133]

The presence of iron in the furnace charge is detrimental. Large amounts of ferric oxide lower the m.p. and melting usually starts in the upper part of the furnace. This causes the electrodes to rise, increases the temperature of the furnace gases and also the dust concentration. The ferric oxide is reduced to iron, which combines with the gaseous phosphorus to form ferro-phosphorus. These reactions increase the electrical energy consumption and also result in a lower thermal efficiency. The reduction of iron compounds occurs at much lower temperatures than are required for the phosphate in the charge. Carbon monoxide reduces $Fe_2O_3$ at above 200°C. to form FeO and the latter is reduced by carbon to form iron at 950°C. Iron phosphate is reduced to $Fe_3P_2$ at temperatures above 600°C.[134] Formation of iron–phosphorus alloys is therefore largely unavoidable in phosphorus furnaces. These alloys usually contain 20–28% of phosphorus, which, from the phase diagram[135] shown in Fig. 7, corresponds to a mixture of $Fe_2P$ and FeP. The quantity of phosphorus discharged from the furnace as ferrophosphorus is about 2–8% of the phosphorus present in the initial feed. It has been proposed to recover this by converting the ferrophosphorus into trisodium phosphate according to the equation[136]:

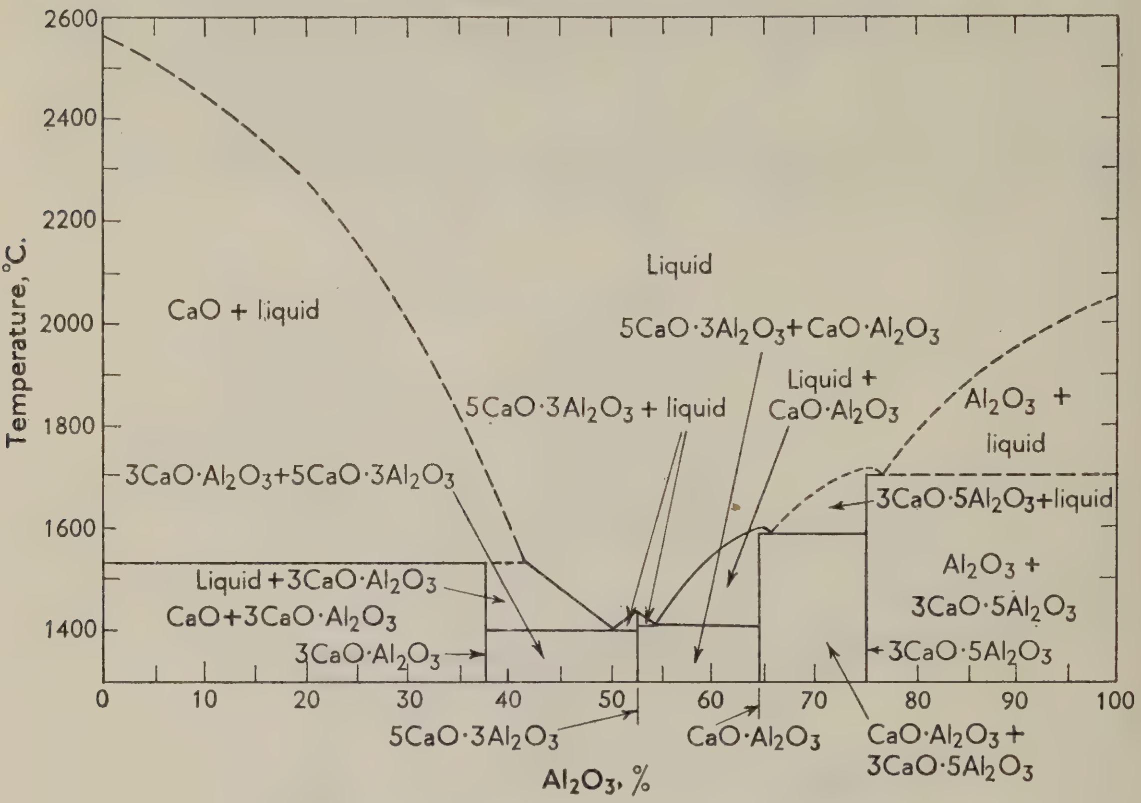

FIG. 6.—Equilibrium diagram for the system CaO–$Al_2O_3$

$$2FeP + 3Na_2CO_3 + 4O_2 = 2Na_3PO_4 + Fe_2O_3 + 3CO_2$$

Alternatively a portion of the phosphorus may be vaporized from ferrophosphorus by melting it in a vacuum.[262]

### THE SLAG

The calcium silicate slag usually contains 3–7% of the phosphorus originally charged into the furnace. The analysis of this material varies with the quality and composition of the raw materials and the method of operation of the furnace. Some typical data are given in Table VIII for plants in operation in England,[86, 137] America[116, 111, 129] and Germany.[95]

*Table VIII.—Typical Percentage Analyses of Phosphorus Furnace Slags*

| | England | U.S.A. | Germany |
|---|---|---|---|
| $P_2O_5$ | 0·5–2·0 | 1·0 | 0·6 |
| $SiO_2$ | 39–43 | 38–40 | 47 |
| CaO | 47–51 | 48–50 | 43 |
| $Fe_2O_3$ | 0·1 | 0·1–0·3 | 0·3 |
| $Al_2O_3$ | 3–5 | 5·9–6·2 | — |
| F | 3–4 | 2–3 | — |

Most slags contain up to 3% of fluorine which may be present as cuspidine, $3CaO,2SiO_2,CaF_2$.[138] About 90% of the fluorine in the furnace comes out in the slag. If the phosphate ore is nodulized or sintered, 30–50% of the fluorine may be volatilized in the process.[86]

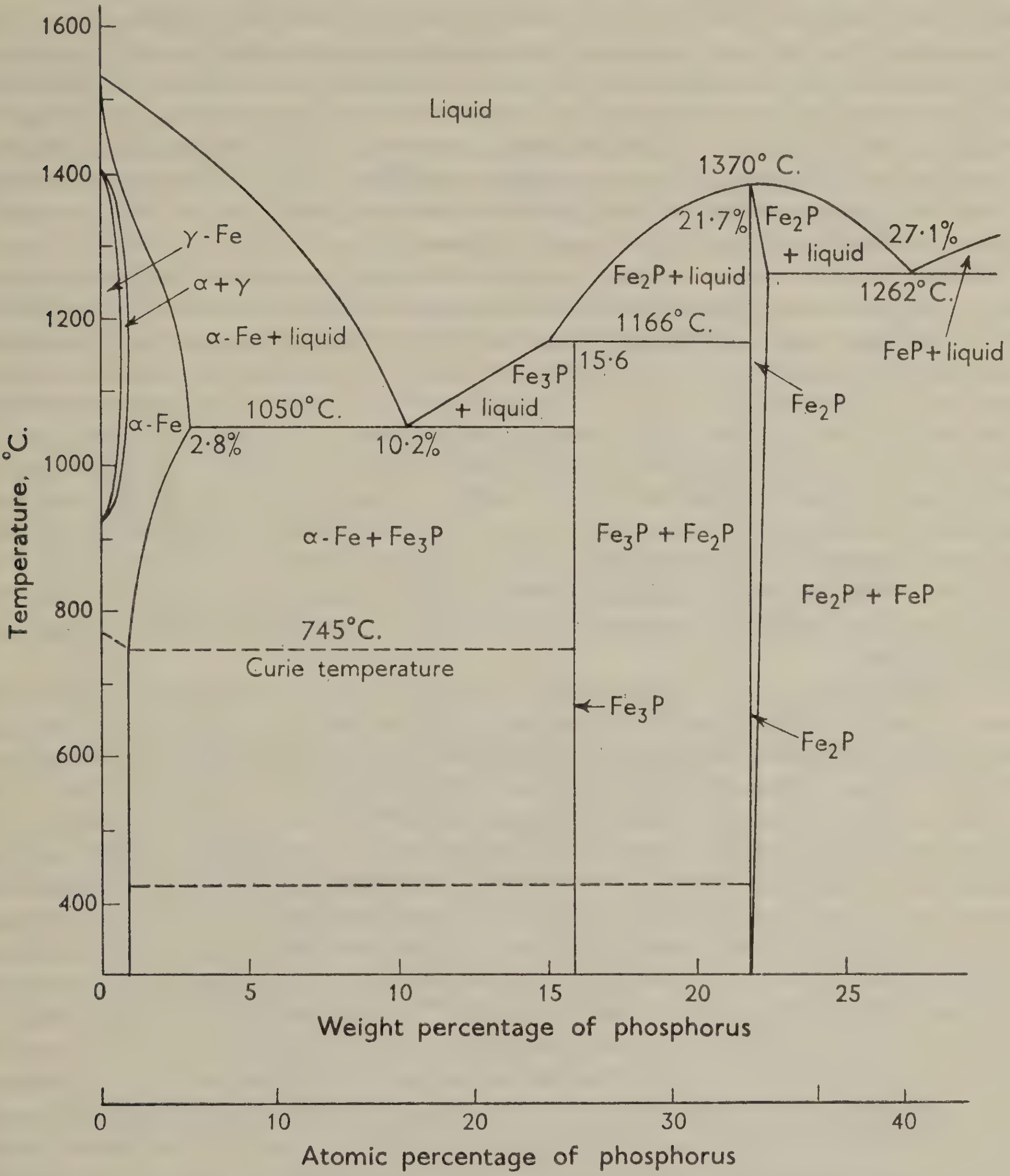

FIG. 7.—Phase diagram of the iron–phosphorus system

### THE FURNACE GASES

The gases leave the furnace at temperatures between 200° and 400°C. A typical composition by volume is: 7–8·5% P, 70–85% CO, 3% $H_2$, 1% $CH_4$, 1% $C_2H_4$, 0·5% $SiF_4$ and 0·5% $CO_2$.[111, 120] A variable amount of dust is also present and this is removed by passing the gases through electrostatic precipitators which operate at discharge potentials as high as 60,000 volts.[120] The partial pressure of the phosphorus vapour in the gases is between 50 and 60 mm. From the vapour pressure equation[139]:

$$\log p_{\text{mm.}} = 18{\cdot}8192 + 1{\cdot}074 \times 10^3 T - 3{\cdot}906 \log T - (3{\cdot}2167 \times 10^3)/T$$

this corresponds to a dewpoint of 170° to 176°C. The furnace gases have therefore to be kept above this temperature in the precipitator unit so as to prevent condensation of phosphorus. The dust which is collected contains some phosphoric acid formed by oxidation and hydration of phosphorus by traces of oxygen and moisture in the equipment. A typical analysis of the dust is[111, 116]: $P_2O_5$ 28–38%, CaO 10–16%, $SiO_2$ 18–20%, $K_2O$ 13–16%, $Na_2O$ 3%, $Al_2O_3$ 3·4%, $Fe_2O_3$ 1·5% and F 6%. The design, construction and operation of precipitator equipment have been described in detail.[116]

After leaving the precipitator the furnace gases are passed through equipment for condensing the phosphorus. This is usually a wet, spray-type condenser or a dry, surface condenser. In both cases they are operated at above the m.p. of phosphorus (44°C.) and molten phosphorus is run to storage under water. For technical details and a discussion of the relative merits of phosphorus condenser systems, reference 116 should be consulted. It has been proposed to recover the phosphorus by means of active charcoal, followed by steam treatment at 200° to 350°C.[140] Aqueous solutions of ammonia and ammonium fluoride have been suggested instead of water as a means of reducing scaling in condenser equipment.[141]

Some of the dust in the furnace gases persists after passing through the precipitators, and becomes emulsified with the phosphorus in the condensers. This forms a mud which contains a significant proportion of the phosphorus in the original raw materials. For example, the mud from the T.V.A. No. 6 furnace described above contained 69% P, 7·6% $P_2O_5$, 3% CaO, 9% F and 1·8% $Fe_2O_3$. This represented 13% of the phosphorus charged to the furnace (see reference 116, page 167). Phosphorus mud appears to be a dispersion of water and colloidal silica or carbon in molten yellow phosphorus. It does not have a sharp melting point, but slowly separates phosphorus when heated below 100° to give a viscous residue containing about 50% P.[255] The phosphorus may be recovered from the mud by vacuum,[142] flash[143] or steam[144] distillation, by centrifugation[254] or by volatilization in a mud furnace. The most convenient method, however, seems to be incorporation with a subsequent furnace charge.

The exhaust gas from the condensers contains about 20% by weight of water when spray-type equipment is used. The volume composition on a dry basis is approximately: 92% carbon monoxide, 5% hydrogen and 2% nitrogen, with minor amounts of carbon dioxide, phosphine and methane. The phosphorus content is about 0·5 lb. per 1000 cu. ft. The calorific value averages 300 B.Th.U. per cu. ft. and the gas may be used as a fuel in other parts of the process,[145] e.g. in kilns for nodulizing the phosphate ore. The use of the gas for synthetic processes, e.g. ammonia or methanol production,[146] has been considered. For this, some purification is necessary in order to remove traces of phosphorus, phosphine, hydrogen sulphide and other unwanted impurities. Several methods have been proposed for removing phosphorus, including absorption in high boiling oils or salt solutions[147] or reaction with phosphate rock[148] or silicofluorides.[149] Phosphorus and phosphine may be removed by catalytic reaction with metals such as copper, iron, titanium or cerium.[150] Oxidation with mixtures of oxygen and nitrogen has been suggested, but this carries with it an explosion hazard. Mixtures of nitric oxide and nitrogen dioxide are safer to use.[151] Chlorine and hypochlorite are alternative oxidizing agents[152] and passing the gas over ferric oxide at temperatures above 250°C. is claimed to be satisfactory.[153] Hydrogen sulphide is removed by washing the gas with a suspension of ferric hydroxide.[147] A product suitable for use in the synthesis of methanol is obtained by mixing a gas containing: CO 75–85%, $CO_2$ 2–5%, $H_2$ 5–7·5%, $N_2$ 10–20%, $CH_4$ 0–2%, $PH_3$ 0·05–0·8% and $H_2S$ 0·04% with half its volume of steam and reacting with siderite ($FeCO_3$) at 350°C. Activation of the latter with CuO is an advantage.[154] Another catalyst which has been used consists of: $Al_2O_3$ 60%, $Fe_2O_3$ 30%, $Cr_2O_3$ 8% and $ThO_2$ 2%.[155] Details have been given (reference 116, page 285) of the oxidation of phosphorus and sulphur by nitric and sulphuric acids, followed by absorption in a packed tower or in a limestone bed. The theory of the condensation of phosphorus in inert gases has been discussed.[156]

### RECOVERY OF BY-PRODUCTS

Recovery and utilization of the various by-products from the electrothermal production of phosphorus have been considered by a number of investigators. The possibility of doing this, however, is limited in most instances by economic considerations. Fluorine is present in the silicate slag, in the precipitator dust and in the phosphorus condensers. Silicofluorides or pure fluorine could be recovered by relatively simple procedures, but this does not appear to be worthwhile.[157] Any vanadium present in the phosphate ore is mostly concentrated in the ferrophosphorus, the concentration in the latter being as high as 5%.[158] One method of recovering this is to roast the ferrophosphorus with sodium carbonate and sodium chloride and then extract the phosphorus and vanadium by leaching with water. Phosphorus is crystallized as trisodium phosphate and the solution hydrolyzed to precipitate vanadium pentoxide. A 95% recovery of both elements is claimed.[159] Vanadium and chromium have been recovered by a three-stage crystallization and hydrolysis process.[160] Attempts have been made to recover uranium from the silicate slag. The best recovery (about 50% of the uranium) was achieved with a high temperature liquid–liquid extraction procedure.[161]

Up to 8 or 9 tons of calcium silicate slag are produced per ton of phosphorus recovered from an electric furnace. Numerous attempts have been made to find an economic outlet for this material. Some of the more important of these are summarized below:

(1) The use of slag for road making is limited by the expense of handling and crushing the material. Its properties as an aggregate for concrete compare well with those of gravel.[108]
(2) Granulated slag as a raw material in the manufacture of Portland cement is satisfactory so far as tensile strength, setting time and other physical properties are concerned. Replacement of some of the $SiO_2$ in the furnace charge by $Al_2O_3$ gives slags which can be converted into aluminous cements. However, the compressive strength of concrete made from these cements may be much lower than that made from commercial products.[116]
(3) As an agricultural material quenched slag has some value as a liming agent, being as effective in this respect as dolomite or limestone.[162] The phosphate present in it has a slight fertilizing action.[163–4]
(4) An expanded slag formed by quenching the molten material with water and steam, and having a cellular structure, can be produced at low cost and is suitable for the construction of concrete blocks.[165]
(5) The production of slag wool as a thermal insulation material has been examined, but does not seem to be competitive with conventional materials.
(6) The manufacture of ceramic bodies and glazes from slag is possible, but the use of the products is limited by the slight radioactivity of the slag.

The main outlet for ferrophosphorus is for the manufacture of special steels. This may necessitate decreasing the proportion of coke in the furnace charge so as to produce a ferrophosphorus of the required quality. Because all the ferrophosphorus produced is not used in steel-making, several alternative uses have been investigated. Roasting with 1·2 parts of limestone for 30–60 min. at 1000° to 1200°C. converts it into a material containing 19–20% $P_2O_5$ which is suitable as an animal feed supplement. The product also has some action as a fertilizer, but is less effective in this respect than superphosphate.[166] The results of animal-feeding tests have been reported.[167] Electrolysis of ferrophosphorus anodes under acid, alkaline or neutral conditions yields soluble iron phosphate, ferric oxide or insoluble iron phosphates, respectively. These products find some application as pigments for anticorrosive paints.[168–9] Alloys containing 3–12% P and 6–20% Si, which are resistant to corrosion by phosphoric, sulphuric and hydrochloric acids, have been made from ferrophosphorus.[116]

The dust recovered from the electrostatic precipitators is valuable as a potash–phosphate type fertilizer.

The technology of the production of phosphorus by the electrothermal process, the selection and composition of raw materials, furnace construction and operation and

**Refs. p. 143**

furnace burden calculations have been discussed in detail.[85, 129] The Tennessee Valley Authority Report No. 3[116] gives a very full account of the chemical engineering involved in the design, operation and development of various types of furnace, and includes many useful data and diagrams.

Typical data, taken from various sources, for weights of raw materials used and products obtained in normal furnace operation are given in Table IX. The figures refer to weight of material per ton of phosphorus produced. For the composition of the materials and other information, the original references should be consulted. The amount of silica used by the T.V.A.[116] is lower than that for other processes because of the very high silica content (24% $SiO_2$) of the T.V.A. phosphate ore. Other data have been reported.[170–1]

*Table IX.—Materials and Products in the Electrothermal Production of Phosphorus*

| Reference | 86 | 116 | 129 | 108 |
|---|---|---|---|---|
| **Raw materials** | | | | |
| Phosphate ore | 7·6 | 11·0 | 10·0 | 7·25 |
| Silica | 3·3 | 0·76 | 1·5 | 2·66 |
| Coke | 1·5 | 1·7 | 1·5 | 1·43 |
| **Products** | | | | |
| Phosphorus | 1 | 1 | 1 | 1 |
| Silicate slag | 8·25 | 8·6 | 8·9 | 7·1 |
| Ferrophosphorus | 0·15 | 0·38 | 0·30 | 0·09 |
| Phosphorus mud | — | 0·25 | — | — |
| Precipitator dust | — | 0·06 | — | — |
| Carbon monoxide | 3·0 | 3·2 | 2·8 | — |

THERMAL EFFICIENCY

The thermal efficiency of the process depends on a number of factors such as the size of the furnace, method of operation, composition of the charge and the amount and composition of the slag. It has been estimated,[102] for example, that a decrease in the $P_2O_5$ content of the phosphate ore from 26 to 25% increases the electrical energy requirement by about 340 kwh. per ton of $P_2O_5$ charged to the furnace. A calculation[116] of the heat balance in a furnace shows that of the electrical energy put in 49%

*Table X.—Thermal Data in Phosphorus Furnace Operation*[116]

| | |
|---|---|
| **Heats of reaction** | |
| $2Ca_3(PO_4)_2+10C = 6CaO+P_4+10CO$ | 4909 B.Th.U./lb. $P_2O_5$ |
| $C+H_2O = H_2+CO$ | 3890 B.Th.U./lb. $H_2O$ |
| $2CaF_2+SiO_2 = 2CaO+SiF_4$ | 2800 B.Th.U./lb. F |
| $Fe_2O_3+3C = 2Fe+3CO$ | 1790 B.Th.U./lb. Fe |
| $CaCO_3 = CaO+CO_2$ | 1790 B.Th.U./lb. $CO_2$ |
| $P_4+5O_2 = 2P_2O_5$ | −8100 B.Th.U./lb. $O_2$ |
| $2CO+O_2 = 2CO_2$ | −2750 B.Th.U./lb. $CO_2$ |
| $Fe+P \rightarrow$ ferrophosphorus | −755 B.Th.U./lb. Fe |
| $CaO+SiO_2 \rightarrow$ slag | −290 B.Th.U./lb. slag |
| **Heat capacity—B.Th.U./lb./°F.** | |
| Slag | 0·3 |
| Condenser exhaust gas | 0·26 |
| Phosphorus at 44°C. | 0·21 |
| **Heat content—B.Th.U./lb.** | |
| Slag at 1450°C. | 810 |
| Ferrophosphorus at 1300°C. | 570 |
| Phosphorus at 44°C. | 25 |

is used in the reaction, 33% is lost as sensible heat and 10% by radiation, conduction and convection. About 8% of the heat could not be accounted for. This was attributed to uncertainty in the thermochemical data, undetermined electrical losses and to the assumptions made as to the composition of the slag and its heat of formation. The sensible heat lost in tapping the slag from the furnace at 1450°C. accounts for about 29% of the electrical energy input, and 58% is required to reduce the phosphate ore. Another estimate[102] gives the distribution of the energy input as 51% for chemical reactions, 35% for sensible heat losses and 9% for radiation, conduction and convection, leaving 5% of the energy unaccounted for. Some useful thermal data are given in Table X, exothermic reactions being indicated by a negative sign.

Some modifications of the electrothermal method of producing phosphorus have been described.[172–3] Operation at temperatures as low as 500°C.[174] and the use of high-frequency current[175] are said to be successful. A high-pressure pump[176] and metering apparatus[177] for use with molten phosphorus have been described. Precautions to be taken to ensure the safe handling of white phosphorus have been outlined,[267] and a sampling technique for molten phosphorus has been suggested.[268]

In many instances the production of phosphorus is coupled with that of phosphoric acid. The development of a continuous process of this type has been reported in detail.[178] The production technology[179–80] and corrosion problems[181] have been discussed. Alternative methods of burning,[182] vaporizing[183] or oxidizing[184] phosphorus have been given.

## Purification of Phosphorus

Phosphorus made by the electrothermal process usually has a purity of 99·8% or more.[86] An American specification for good quality material is[85]:

| | |
|---|---|
| Insoluble in benzene | 0·006–0·025% |
| Oil | 0·001–0·020% |
| Arsenic as $As_2O_3$ | 50–180 p.p.m. |
| Iron as Fe | 1–8 p.p.m. |
| Fluorine as F | 1–4 p.p.m. |

Technical grade yellow phosphorus is less pure and the impurities in this have been given as[185]:

| | |
|---|---|
| Arsenic as As | 40–113 p.p.m. |
| Sulphur as S | 5–10 p.p.m. |
| Iron as Fe | 3–20 p.p.m. |
| Magnesium as Mg | 1–3 p.p.m. |
| Antimony as Sb | 130–135 p.p.m. |
| Silicon as Si | 5000–10,000 p.p.m. |
| Carbon as C | 50–1400 p.p.m. |
| Fluorine as $F_2$ | 7 p.p.m. |

Up to 5 p.p.m. of calcium and copper, and traces of lead and manganese may also be present.

Various methods of purification have been described. The procedures used depend on the quality of the phosphorus required, the purest material being that used in semiconductors. Stirring molten yellow phosphorus with a dilute solution of sodium or potassium dichromate acidified with sulphuric acid removes traces of phosphorus pentoxide, calcium oxide, fluorine, iron and some organic matter.[116] A white or colourless phosphorus is obtained by filtering the liquid through a bed of active carbon. Heating phosphorus for a short time at 70°C. in an inert atmosphere with a small percentage of polyphosphoric acid (75–85% $P_2O_5$) and then filtering through active carbon and Fullers earth reduces the organic impurities (hydrocarbons and phenols) to less than 0·01% and the inorganic impurities (As, Pb, Fe, Mn, Si, Ca and Mg) to 0·005%.[186]

Most of the arsenic can be removed by steam distillation, but to reduce the content to 5 p.p.m. of $As_2O_3$ or less requires a multistage process.[187] Purification of crude phosphorus by solvent extraction[188] or by distillation in an inert atmosphere alone[189] or in the presence of active charcoal[273] has been suggested.

Several procedures have been described for obtaining very pure phosphorus for use in preparing semiconductors. In one method phosphorus is heated in contact with silver, cobalt, copper, chromium, iron or molybdenum at 200° to 900°C. This gives the metal phosphide which is then decomposed at a higher temperature or a lower pressure to give phosphorus of semiconductor purity.[190] Arsenic, sulphur or selenium can be removed by heating phosphorus under reflux with lead or aluminium.[274] Electrodialysis[275] or agitation[276] of phosphorus with dilute nitric acid also effects purification. Technical yellow phosphorus can be purified by filtering at 90°C., stirring with 20% potassium hydroxide, cooling and then removing the alkali. The phosphorus is then heated to 50°C. in a nitrogen atmosphere and stirred with 5% sulphuric acid, then with water, and finally it is distilled at 100°C. and 2 mm. pressure. Most of the halogens, sulphur, arsenic, silicon, copper, magnesium, calcium, antimony and iron are removed by this treatment. The carbon content is reduced to below 20 p.p.m. by passing phosphorus vapour over quartz at 900° to 1200°C. and chilling. Much red phosphorus is formed during this operation, and is removed by distilling or filtering. The white phosphorus is then vacuum distilled, the first 10% being rejected and the next 30% is recovered.[185] A further reduction to below 5 p.p.m. of carbon is achieved by vaporizing the purified phosphorus at 90° to 300°C. and 0·1–100 mm. pressure followed by heating at 800° to 1200°C. for 0·1–10 sec. in the presence of quartz. This decomposes hydrocarbons, deposits carbon on the quartz, and phosphorus is condensed out of the system.[191] The technique of zone refining has also been used to purify phosphorus, heat being applied by a heated perforated iron slug, moved magnetically.[277] Typical values for the trace elements in highly-purified phosphorus are[185]:

| | |
|---|---|
| Calcium | 0–4 p.p.m. |
| Copper | 0·2 p.p.m. |
| Magnesium | 0·1–0·9 p.p.m. |
| Carbon | < 5 p.p.m. |
| Silicon | 2–4 p.p.m. |
| Antimony | 0·5 p.p.m. |
| Arsenic | 15–40 p.p.m. |
| Sulphur | nil |
| Iron | nil |
| Halogens | nil |

Pure red phosphorus has been obtained by heating pure white phosphorus to 200°C. and then raising the temperature in steps of 50° to 350°C. over a period of four days. After 48 hr. at 350°C. the product is slowly cooled to give red phosphorus containing the minimum amount of the white variety[185] (see also p. 138).

Heating red phosphorus at 70–95°C. with a 3–5% solution of a mineral acid and then distilling at $10^{-2}$ to $10^{-4}$ mm. pressure is claimed to reduce the total iron, aluminium, copper and silicon content from above 80 p.p.m. to 5 p.p.m.[192] Evaporating red phosphorus in a vacuum at 900° to 950°C. or in the presence of hydrogen, helium or argon and then condensing in a quartz tube is said to give pure phosphorus.[193]

Potassium, calcium, iron, manganese and copper are removed by heating red phosphorus with 10% potassium hydroxide solution, drying the phosphorus and then vacuum distilling at 400°C. The distillate is then heated for several days at 300°C. in a sealed quartz tube to convert it into red phosphorus. This is again converted into white phosphorus by distilling it in the presence of metallic indium and allowing it to stand in contact with indium for one day at 150°C. The product is finally distilled at 300°C. to convert it into red phosphorus of 99·9999% purity, containing 1–2 p.p.m. of silicon and magnesium.[194] Oxide impurities in trace amounts are often present in phosphorus which has been purified by sublimation in hydrogen, by zone melting or by vacuum distillation. These are reduced to a minimum by subliming red phosphorus at 300° to 380°C. and $4 \times 10^{-5}$ mm. pressure and then redistilling the white phosphorus in quartz at 150°C. Titanium metal is used to absorb traces of oxygen in the apparatus.[195]

### Chemical Reactions in the Phosphorus Furnace

The formation of phosphorus by the reaction of fluorapatite with carbon and silica in the temperature range 1400° to 1600°C. can be represented approximately by the equation[86]:

$$2Ca_{10}(PO_4)_6F_2 + 18SiO_2 + 30C = 3P_4 + 2CaF_2 + 18CaSiO_3 + 30CO$$

If variations in the lime:silica ratio in the furnace charge are taken into account, the following generalized equation may be written[129, 196]:

$$\begin{aligned}(4+4y)Ca_5(PO_4)_3F + (20x+1-9y)SiO_2 + (30+30y)C \\ = 20(CaO,xSiO_2,yCaF_2) + (1-9y)SiF_4 + (30+30y)CO + (3+3y)P_4\end{aligned}$$

The mechanism of the reduction has been the subject of much investigation. Various explanations have been given, but there seems to be insufficient experimental evidence to establish any one of them conclusively.

At high temperatures silica and, to a lesser extent, alumina act as strong acids in the decomposition of phosphate rock. Silica and tricalcium phosphate start to react at about 1150°C. and at 1630°C. the compound $Ca_3P_2O_8,3SiO_2$ is said to be formed. This compound is readily reduced by carbon.[133] Silica alone does not form elemental phosphorus when it reacts with phosphate rock at furnace temperatures, but at higher temperatures (above 1800°C.) some phosphorus pentoxide may be liberated (reference 116, page 3).

When carbon and silica are both present the latter accelerates the sublimation of phosphorus from fluorapatite and also lowers the temperature at which this occurs. At 1600°C. phosphorus is completely volatilized in 1 hr. on heating fluorapatite with wood charcoal in the presence of 1% of silica. If the amount of silica is increased to give a $SiO_2$:CaO ratio of 1·07 in the system, the same result is obtained at temperatures as low as 1350°C. Silica and carbon are also necessary for the removal of fluorine from fluorapatite. None of this element is volatilized at 1600°C. when only carbon is present. However, with the addition of silica as much as 50% of the fluorine can be removed in 1 hr. at 1450°C.[82]

Most of the investigations into the reactions occurring in the phosphorus furnace have been carried out with tricalcium phosphate. It is well established that the reaction of this material with carbon and silica at temperatures between 1000° and 1600°C. is represented by the equation:

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 = \tfrac{1}{2}P_4 + 3CaSiO_3 + 5CO$$

The heat required for this reaction is very close to that calculated for the above equation, when a blast furnace process is used.[197]

In the absence of silica the net effect is:

$$2Ca_3(PO_4)_2 + 10C = P_4 + 6CaO + 10CO$$

Various figures between 1000° and 1400°C. have been given for the temperature at which tricalcium phosphate is reduced by carbon. This may be as low as 1100°C., but at this temperature the reaction is very slow.[198] It is also necessary to consider the temperature in relation to the amount of silica present, because this compound lowers the reaction temperature. For example, it is reported[199] that 90% of the phosphorus is volatilized in 1 hr. at 1300°C. from a mixture of equal weights of coke and phosphate rock. However, this mixture contained 7·5% of silica, derived from the coke and the rock. On the other hand if silica is absent phosphorus is volatilized from a mixture of carbon and tricalcium phosphate at a rate of 45% in 1 hr. at 1300°C., 96% at 1400°C. and 100% at 1550°C. In small scale experiments using pure carbon flour and tricalcium phosphate, volatilization of phosphorus was found to start at 1150°C.

The effect of the amount of carbon is shown in Table XI for mixtures heated for 1 hr. at 1400°C.[127]

Rates of reaction in the temperature range 1200° to 1500°C. have been measured[127] for mixtures of tricalcium phosphate and carbon and also for mixtures containing added silica and alumina.[200] The rate of reaction was found to be first order with respect to the tricalcium phosphate. The values of $k$ in the first order equation $kt = \log_e(a/a-x)$ were calculated with the results shown in Table XII.

*Table XI.—The Effect of Carbon to Phosphorus Ratio on the Volatilization of Phosphorus from Tricalcium Phosphate in 1 hr. at 1400°C.*

| Weight ratio $C:P_2O_5$ | Phosphorus volatilized % |
|---|---|
| 0·383 | 82·2 |
| 0·543 | 88·6 |
| 0·933 | 95·2 |
| 2·188 | 99·8 |

Because these reactions are first order it was suggested that the mechanism of the reduction involved the dissociation of tricalcium phosphate into lime and phosphorus pentoxide, followed by the reduction of the latter by carbon:

$$Ca_3(PO_4)_2 \rightleftharpoons 3CaO + P_2O_5$$
$$P_2O_5 + 5C \doteq 5CO + P_2$$

*Table XII.—First-order Velocity Constants for the Reduction of Tricalcium Phosphate*[127]

| Temp. °C. | Velocity constant, $k$ mm.$^{-1}$ C alone | $C+SiO_2$ | $C+Al_2O_3$ |
|---|---|---|---|
| 1200 | 0·00346 | 0·0167 | — |
| 1250 | 0·01126 | 0·0492 | — |
| 1300 | — | 0·1257 | 0·0682 |
| 1400 | 0·0747 | — | — |
| 1500 | 0·329 | — | — |

It was observed that the reduction of phosphorus pentoxide started at 800°C. On this basis it was concluded that this reaction would be rapid at 1200°C., so that the rate-determining step in the reduction of the tricalcium phosphate is the dissociation of the latter.[127] However, it has also been reported that substantially no reduction of phosphorus pentoxide by carbon occurs at temperatures below 1200°C.[201] Since this reduction takes place between solids at the lower temperatures, the explanation of the two observations may be that in one of them[127] a considerable excess of carbon was used. Analysis of samples taken from a phosphorus furnace during overhaul showed that no appreciable volatilization of phosphorus from the phosphorite occurs until it has melted, probably by slagging with silica.[266] Carbon monoxide does not reduce phosphorus pentoxide to any extent under normal furnace conditions, but it is possible that any carbon monoxide formed by reduction of the pentoxide may act as a catalyst in some other reaction. No dissociation of tricalcium phosphate was observed on heating it in a vacuum for 1 hr. at 1300° to 1400°C.[128] In the presence of carbon, therefore, the following reaction can occur:

$$2Ca_3(PO_4)_2 + 10CO = 6CaO + 10CO_2 + P_4$$

The action of silica in accelerating the reduction of phosphate rock by carbon has been known since 1826,[202–3] but no systematic examination of this was carried out for a century. The effect of variations in the flux:lime ratio on the volatilization of phosphorus from mixtures containing equal weights of tricalcium phosphate and carbon is shown in Fig. 8.[200]

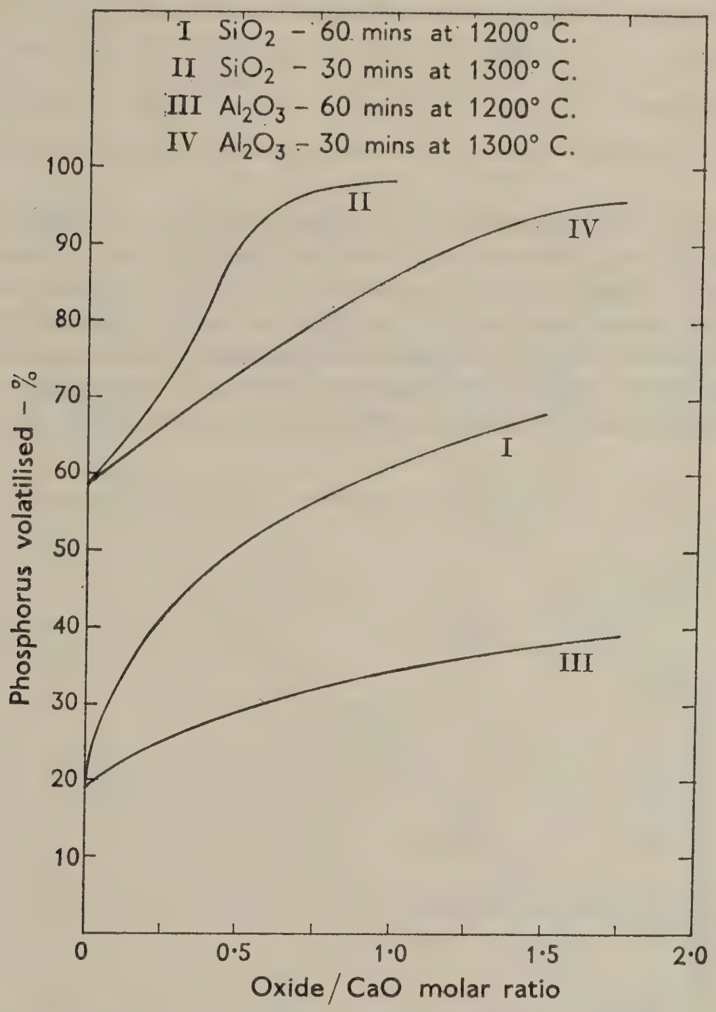

FIG. 8.—The effect of silica and alumina on the reduction of tricalcium phosphate with an equal weight of carbon[200]

For a constant molar $Ca_3(PO_4)_2:SiO_2$ ratio of 1:3 the amount of phosphorus volatilized increased with the amount of carbon in the mixture as shown in Fig. 9. These results indicate that silica promotes the reduction to a greater extent than alumina does. It is also evident that no phosphorus is formed with silica alone. The effect of temperature is given in Table XIII for a mixture containing equal weights of carbon and tricalcium phosphate and having a molar $CaO:SiO_2$ ratio of 1:1. The time of heating was 1 hr. at every temperature.

*Table XIII.—Effect of Temperature on the Reduction of Tricalcium Phosphate in the Presence of Molar Quantities of Silica and Carbon*[200]

| Temperature °C. | 1050 | 1100 | 1150 | 1200 | 1250 |
|---|---|---|---|---|---|
| % P volatilized | 1·0 | 11·7 | 28·4 | 61·6 | 95·3 |

**Refs. p. 143**

A naturally-occurring aluminium phosphate, wavellite, was found to be more readily reduced than tricalcium phosphate when heated with an equal weight of carbon for 1 hr. at various temperatures. The percentages of phosphorus volatilized are given in Table XIV.

*Table XIV.—Reduction of Aluminium Phosphate Ore with Carbon*

| Temperature °C. | 1050 | 1100 | 1150 | 1200 | 1300 | 1400 |
|---|---|---|---|---|---|---|
| % P volatilized | 5·4 | 71·9 | 83·2 | 83·9 | 88·6 | 90·2 |

The decrease in the rate of reduction at temperatures above 1150°C. was attributed to the formation of iron phosphide as a result of the high iron content of the ore.[200]

The reduction of phosphate rock by carbon in the presence of silica has also been shown to be a first-order reaction.[116] The reaction rate is indicated in Fig. 10.

These data give lower velocity constants than those for the reduction of tricalcium phosphate (Table XII). This is in agreement with other observations[83, 134, 204] that the phosphorus pentoxide in tricalcium phosphate is more easily reduced by carbon than that in fluorapatite. The breaks in the graphs shown in Fig. 10 were attributed to reaction between the melt and carbon which had segregated in it.[116]

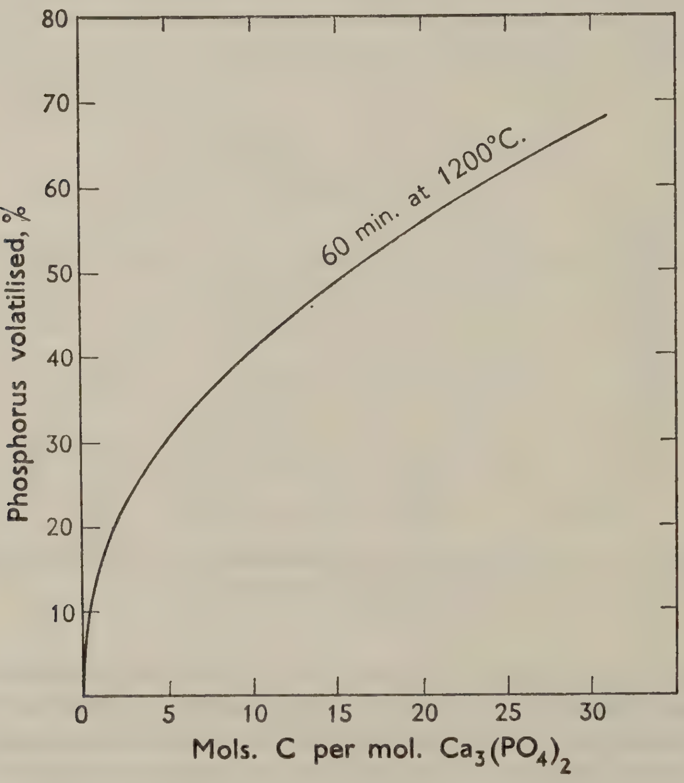

FIG. 9.—The effect of carbon on the reduction at 1200°C. of a mixture having a constant molar $Ca_3(PO_4)_2/SiO_2$ ratio of 1:3[200]

Equilibrium constants have been calculated[92, 199] for a number of reactions involving tricalcium phosphate. Table XV gives the temperatures at which the equilibrium pressure of the reaction gases is 1 atm.

The data in Table XV were calculated from the Nernst approximation formula:

$$\log K_{p(\mathrm{atm.})} = -\frac{\Delta H}{4{\cdot}57T} + \Sigma\,\nu\,.1{\cdot}75\log T + \Sigma\,\nu c$$

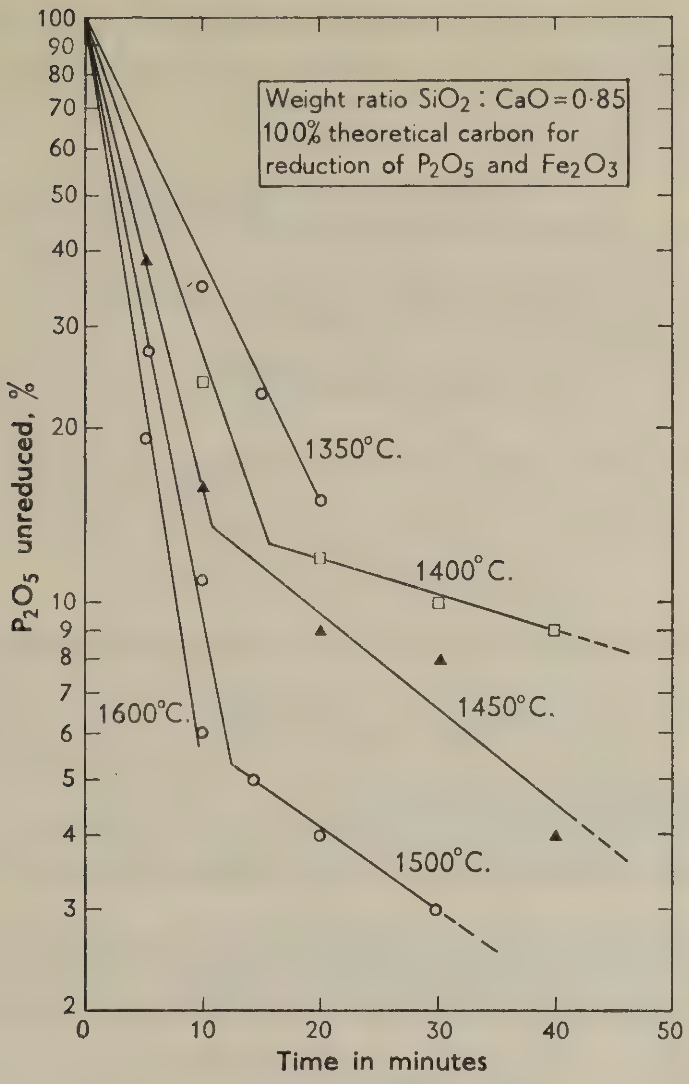

FIG. 10.—Rate of reduction of $P_2O_5$ in brown rock phosphate when heated with carbon

*Table XV.—Equilibrium Pressures for Reactions of Tricalcium Phosphate*

| Reaction | Temp. °C. for 1 atm. pressure | |
|---|---|---|
| | Ref. 92 | Ref. 199 |
| $Ca_3(PO_4)_2 + 5C = P_2 + 3CaO + 5CO$ | 1370 | 1385 |
| $Ca_3(PO_4)_2 + 5C = \frac{1}{2}P_4 + 3CaO + 5CO$ | 1420 | — |
| $Ca_3(PO_4)_2 + 8C = Ca_3P_2 + 8CO$ | — | 1690 |
| $Ca_3(PO_4)_2 + 8C = P_2 + 3Ca + 8CO$ | — | 1680 |
| $Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$ | 2400 | 2310 |
| $Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + \frac{1}{2}P_4O_{10}$ | 4000 | — |
| $Ca_3(PO_4)_2 + 2SiO_2 = Ca_3Si_2O_7 + P_2O_5$ | — | 2390 |
| $Ca_3(PO_4)_2 + SiO_2 = Ca_3SiO_5 + P_2O_5$ | — | 2860 |
| $2Ca_3(PO_4)_2 + 3SiO_2 = 3Ca_2SiO_4 + 2P_2O_5$ | | 2550 |
| $Ca_3(PO_4)_2 + 5C + 3SiO_2 = P_2 + 3CaSiO_3 + 5CO$ | 1050 | 1190 |
| $Ca_3(PO_4)_2 + 5C + 3SiO_2 = \frac{1}{2}P_4 + 3CaSiO_3 + 5CO$ | 1082 | — |
| $Ca_3(PO_4)_2 + 5C + 2SiO_2 = P_2 + Ca_3Si_2O_7 + 5CO$ | 1180 | 1200 |
| $Ca_3(PO_4)_2 + 5C + SiO_2 = P_2 + Ca_3SiO_5 + 5CO$ | — | 1280 |
| $2Ca_3(PO_4)_2 + 10C + 3SiO_2 = 2P_2 + 3Ca_2SiO_4 + 10CO$ | — | 1260 |
| $Ca_3(PO_4)_2 + 5C + 3Al_2O_3 = P_2 + 3CaAl_2O_4 + 5CO$ | 1260 | — |
| $Ca_3(PO_4)_2 = 3CaO + P_2O_5$ | 4300 | — |

### POSSIBLE FORMATION OF CALCIUM PHOSPHIDE AND CARBIDE

There is some evidence that the formation of calcium phosphide could be involved in the mechanism of the reaction and that interaction of this with tricalcium phosphate gives phosphorus according to the equations[128]:

$$\begin{aligned} Ca_3(PO_4)_2+8C &= Ca_3P_2+8CO \\ 5Ca_3P_2+3Ca_3(PO_4)_2 &= 8P_2+24CaO \end{aligned}$$

From the data the equilibrium pressure of carbon monoxide in the first of these reactions is given in atmospheres by the equation[205]:

$$\log p = 9 - \frac{16{,}480}{T}$$

This gives a pressure of 1 atm. at 1540°C. For the second reaction the pressure is given by:

$$\log p = 4{\cdot}532 - \frac{8190}{T}$$

which leads to a value of 1 atm. at about 1550°C. The pressure equation for the total reaction is:

$$\log p = 4{\cdot}841 - \frac{8480}{T}$$

which gives a pressure of 1 atm. at 1480°C.

The second of the above reactions is reversible and at temperatures below 900°C phosphorus vapour combines with lime to form calcium phosphide.[205]

*Table XVI.—Volatilization of Phosphorus from Tricalcium Phosphate and Carbon at* 1200°*C.*–1840°*C.*

| Temp. °C. | Time min. | Reaction products % | | | | | |
|---|---|---|---|---|---|---|---|
| | | $Ca_3(PO_4)_2$ | $Ca_3P_2$ | $CaC_2$ | $CaCN_2$ | CaO | P |
| 1200 | 30 | 87·6 | — | — | — | — | 12·4 |
| 1430 | 30 | 1·6 | — | 1·7 | 0·3 | 96·4 | 98·3 |
| 1530 | 30 | 0·7 | 0·15 | — | — | — | 99·0 |
| 1620 | 45 | 1·5 | 1·1 | 2·9 | 27·7 | 66·8 | 96·6 |
| 1640 | 60 | 2·0 | 1·2 | 7·4 | 42·3 | 47·0 | 95·9 |
| 1735 | 45 | 2·0 | 3·7 | 32·9 | 22·2 | 39·2 | 91·8 |
| 1820 | 30 | 0·4 | 8·5 | 46·8 | 23·4 | 20·9 | 85·0 |

Experiments in which carbon was heated with 1·7 parts by weight of tricalcium phosphate in a stream of nitrogen indicated that the optimum temperature for volatilization of phosphorus was 1550°C. Calcium phosphide in the solid residue was less than 5% at temperatures below 1750°C. The results are summarized in Table XVI from which it will be seen that appreciable amounts of calcium carbide and calcium cyanamide are formed at temperatures above 1600°C. The formation of calcium carbide may be due to reaction of lime with the excess of carbon present, according to the equation[82, 128]:

$$CaO+3C = CaC_2+CO$$

The equilibrium pressure for this reaction is 1 atm. at 1780°C. The carbide is also formed from calcium phosphide and carbon, a reaction which is exothermic at 590°C.[205]:

$$Ca_3P_2+6C = 3CaC_2+P_2$$

The equilibrium constant in atmospheres is given by:

$$\log K_p = \frac{-77{,}500}{4{\cdot}57T} + 1{\cdot}75 \log T + 3{\cdot}0$$

for which the pressure is 1 atm. at 1660°C. Experiment showed that decomposition of calcium phosphide is incomplete at 1470°C.

Tricalcium phosphate reacts with calcium carbide according to the equation:

$$Ca_3(PO_4)_2 + 8CaC_2 = Ca_3P_2 + 8CaO + 16C$$

This appears to be followed by reaction of the phosphide with tricalcium phosphate, because on heating at 1200–1400°C. the product contains 74% CaO, 15% C and 3% tricalcium phosphate.

### REDUCTION BY CARBON MONOXIDE

The reduction of tricalcium phosphate by carbon monoxide:

$$Ca_3(PO_4)_2 + 5CO = 3CaO + 5CO_2 + P_2$$

has been considered[127] as a possible reaction in the formation of phosphorus. The evidence for this is conflicting. From a study of the phosphate–carbon–silica system[133] it was reported that there was no reaction with carbon monoxide at 1400° to 1600°C. The heat of reaction has been estimated to be −219 kcal.[92] Assuming that the Nernst approximation formula applies, this heat leads to an equilibrium pressure of 1 atm. at above 2000°C. In the presence of silica the heat change for the reaction:

$$Ca_3(PO_4)_2 + 5CO + 3SiO_2 = P_2 + 5CO_2 + 3CaSiO_3$$

is given as −134·7 kcal. which corresponds to 1 atm. pressure at 3000°C. More recently[206] it has been reported that on heating mixtures of tricalcium phosphate and carbon at 850–1150°C. *in vacuo* the rate of reduction ($V$) in mg./hr. per g. of material is given by:

$$\log V = \frac{-47{,}100}{4{\cdot}575T} + 8{\cdot}96$$

From a comparison with data obtained on the reduction of oxides by carbon, and because the energy required for all these reactions is very nearly the same as that for the reduction of carbon dioxide by carbon, it is suggested that the mechanism for the tricalcium phosphate–carbon monoxide reaction is represented by the following reactions, of which the second is the rate-determining step:

$$Ca_3(PO_4)_2 + 5CO = 3CaO + 5CO_2 + P_2$$
$$CO_2 + C = 2CO$$

At temperatures of 1200–1400°C. it has been observed (reference 116, page 11) that the rate of reduction of phosphate rock by carbon and silica in an atmosphere of carbon monoxide varies directly with the rate of flow of gas. In 1 hr. at 1300°C. the amount of phosphorus volatilized was 33% and this increased to 52% when the carbon monoxide was replaced by nitrogen. No volatilization of phosphorus occurred at 1300°C. when the rock was heated in carbon monoxide in the absence of carbon.

### VOLATILIZATION OF SILICON

Volatilization of silica can occur in the phosphorus furnace. It is possible that this may be volatilization of silicon monoxide formed during the reduction process. Silica is reduced by carbon at temperatures above 1500°C. according to the equation[207]:

$$SiO_2 + C \rightleftharpoons CO + SiO$$

Silicon monoxide is also formed by reaction of silica with silicon. It is unstable at temperatures below about 1200°C.[208] and with carbon monoxide it forms silicon carbide:

$$3SiO + CO = 2SiO_2 + SiC$$

Tricalcium phosphate is reduced by silicon monoxide at 1350°C.[207]:

$$2Ca_3(PO_4)_2 + 10SiO = P_4 + 3Ca_2SiO_4 + 7SiO_2$$

A mechanism for the reduction of phosphate which involves silicon monoxide seems to be less likely than the others which have been proposed. The vapour pressure of silicon monoxide in the presence of silica at 1570°C. is about $3 \times 10^{-2}$ mm.[209–10] The heat of formation of silicon monoxide from silicon and silica is about +164 kcal. and from carbon and silica it is about +160 kcal.[207, 211]

The experimental evidence suggests that carbon monoxide has only a minor role in the reduction. The same applies to the hypothesis of the dissociation of tricalcium phosphate into calcium oxide and phosphorus pentoxide followed by reduction of the latter.

## RED PHOSPHORUS

### PREPARATION

The red variety of phosphorus, generally referred to as amorphous, is manufactured substantially by the method previously described (Mellor, VIII, 746). This is usually a batch process in which white phosphorus is heated in a closed cast iron or steel vessel at temperatures above 250°C. The reaction is exothermic and the temperature must be carefully controlled in the initial stages.[86] At the end of the reaction the temperature is kept at 400°C. for several hours. The solid product is dug out, ground under water and boiled with sodium carbonate to remove unchanged white phosphorus. It is then filtered and vacuum dried. The material can be stabilized against oxidation by suspending it in a 1% solution of sodium aluminate. Magnesium and zinc oxides have a similar effect.[212] The resistance to oxidation is also improved by removing the iron and copper impurities by boiling with 8% sodium cyanide solution.[213] Other methods which have been suggested include boiling with hydrochloric, sulphuric or nitric acid,[214] heating in moist air at 40° to 90°C. followed by washing[215] and coating the particles with concentrated phosphoric acid.[216]

Copper, iron, bismuth, silver and nickel have been shown to increase the oxidation rate greatly. Cadmium and tin have a smaller effect, lead and chromium very little, and aluminium and zinc reduce the oxidation rate. The best procedure for stabilization appears to be boiling for 4–6 hr. with 5% sulphuric acid to remove iron, followed by boiling for ½ hr. with a solution containing 5% of sodium cyanide and 1·5% of sodium hydroxide. 0·5–7% of aluminium hydroxide is then precipitated on the phosphorus.[217]

In order to avoid the troublesome procedure of having to break up the product, a ball mill procedure has been suggested.[218] A continuous process has been developed[219] in which white phosphorus is heated at its boiling point until the conversion is about 50% complete. Under these conditions (approximately 6·5 hr. at 280°C.) the reaction mixture remains fluid with the red phosphorus suspended in it. To prevent volatilization of phosphorus the temperature must be kept below 285°C. The red phosphorus is separated by sedimentation and traces of white phosphorus are removed by heating at 200°C. in a stream of carbon monoxide, or by solvent extraction or flash, vacuum or steam distillation.[220] Other procedures, involving purification at 250°C.[221] and 300° to 350°C.[222] have been suggested. Oxidation with air[223] or dilute hydrogen peroxide[224] is said to remove both iron and white phosphorus. Apparatus for the continuous process has been described.[225]

Various other procedures have been suggested, including heating white phosphorus under reflux at 220° and 240°C. in a liquid such as diphenyl,[226] passing phosphorus through molten lead,[227] subjecting phosphorus vapour to the action of nitrogen oxides, iodine or bromine[228] or an electric discharge,[229] atomizing phosphorus in a closed chamber at 300° to 450°C.,[230] heating phosphorus in a closed container, under a strictly controlled temperature regime at up to 275° and subsequently to 325° to 340°,[283] and exposing a solution of phosphorus in carbon disulphide to ultra-violet light.[231] It has also been proposed to heat phosphorus vapour at 400° to 500°C. under 10–25 atm. pressure and then to cool it by rapid expansion.[232]

The reaction of phosphorus tribromide with magnesium, zinc or aluminium powder in anhydrous ether is said to give red phosphorus of 99% purity[233] (see also page 156). Small yields are also reported from the reaction in the presence of an electric discharge between hydrogen and phosphorus trichloride, phosphorus oxychloride or phosphorus tribromide.[234]

### MECHANISM OF THE CONVERSION

The mechanism of the conversion of white into red phosphorus has been studied by a number of investigators. The effect of time on the conversion when white phosphorus is heated in sealed glass ampoules is shown in Table XVII.[235] Red phosphorus, lime, silica gel, iron, selenium, $Fe_2O_3$ or $U_3O_8$ failed to catalyze the reaction.

*Table XVII.—Effect of Time and Temperature on the Conversion of White to Red Phosphorus*[235]

| Temp. °C. | Time hr. | % red P formed |
|---|---|---|
| 220–250 | 3 | 17 |
| 220–250 | 47 | 69 |
| 320–350 | 18 | 72 |
| 320–350 | 26 | 76 |
| 400 | 1¼ | 100 |
| 500 | 1 | 100 |

Observations in the temperature range 176–373°C. showed that the conversion is a first-order reaction below 263°C. At the higher temperatures the rate increases, suggesting that the reaction is autocatalytic.[236] A later investigation gave no indica-

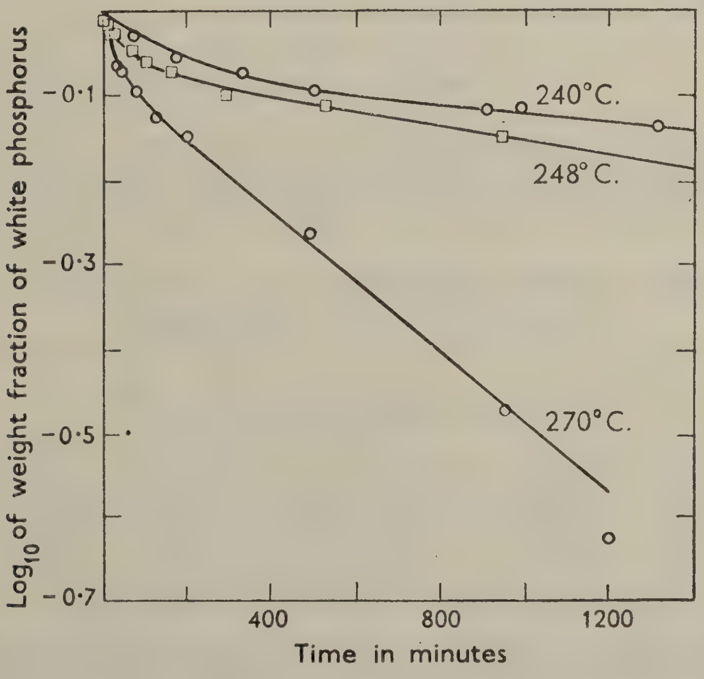

FIG. 11.—Rates of conversion of white to red phosphorus in the presence of 0·05% of iodine

tion of the reaction being autocatalytic and at temperatures in the range of 250–400°C. the first order velocity constant in min.$^{-1}$ was given by the equation:

$$\log_{10} k = -\frac{8470}{T} + 12{\cdot}62$$

which gives an activation energy of 38,700 g.-cal./mole. In the presence of iodine or sulphur as catalysts the rates of conversion are as shown in Figs. 11 and 12 respectively.

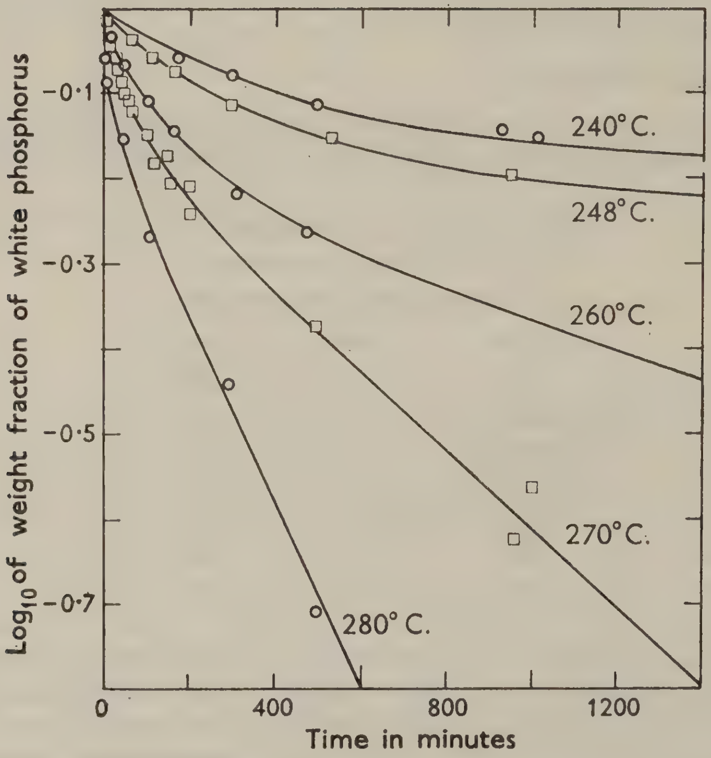

FIG. 12.—Rates of conversion of white to red phosphorus in the presence of 1·0% of sulphur

The rates of the catalyzed reactions are given by:

$$-2{\cdot}303 \log \frac{m}{m_0} = k_1 t + k_2 c(1 - e^{-k_3 t})$$

where $m/m_0$ is the fraction of white phosphorus remaining at time $t$, $c$ is the initial concentration of catalyst, $k_1$ is the first-order velocity constant for the uncatalyzed reaction, $k_2$ the constant for the formation of red phosphorus and $k_3$ is the constant for the disappearance of the catalyst. $k_2$ is independent of temperature and has an average value of 500 for iodine as catalyst, and 50 for sulphur. The values obtained for $k_3$ are given in Table XVIII and Table XIX.

*Table XVIII.—Velocity Constant, $k_3$ min.$^{-1}$, for the Iodine-catalyzed Conversion of White to Red Phosphorus*

| Mol. fraction $\frac{I_2}{P_4} \times 10^3$ | $k_3$ min.$^{-1} \times 10^3$ | | |
|---|---|---|---|
| | 240°C. | 248°C. | 270°C. |
| 0·0489 | 7·81 | 17·9 | — |
| 0·244 | 3·47 | 14·0 | 36·6 |
| 0·489 | — | 25·2 | 64·8 |

In the initial stages of the reaction and up to 50% conversion of the white phosphorus, the mixture remains fluid. It then becomes rapidly viscous and passes through a plastic state before solidifying. Between 6 and 10% conversion the reaction mixture contains particles of red phosphorus, about 20 to 30 microns in diameter, suspended in it. These grow in size and number until they touch and form an interlocking mass.[237] Between 6 and 60% conversion at 280°C. the particles increased from 1 to 150 microns in diameter, the average size being 26 to 60 microns. The specific surface as measured by adsorption of propane at −78·6°C. is found to be inversely proportional to the percentage conversion of white to red phosphorus. The mechanism proposed for the reaction is an initial formation of nuclei of red phosphorus according to a first-order law. The nuclei then agglomerate to form aggregates which give rise to a porous three-dimensional network. There is no evidence of chain formation.[238] It has been pointed out that this mechanism agrees with the kinetic data, if during the production of nuclei the phosphorus atoms are rearranged, without dissociation of $P_4$ molecules, to form red phosphorus molecules which are more compact than those of the white phosphorus from which they are formed.[139] In the initial stages of the iodine and sulphur catalyzed reactions a chain mechanism, which is independent of temperature, appears to be involved.

*Table XIX.—Velocity Constant, $k_3$ min.$^{-1}$, for the Sulphur-catalyzed Conversion of White to Red Phosphorus*

| Mol. fraction $\frac{S_8}{P_4} \times 10^3$ | $k_3$ min.$^{-1} \times 10^3$ | | | | |
|---|---|---|---|---|---|
| | 240°C. | 248°C. | 260°C. | 270°C. | 280°C. |
| 2·42 | 0·85 | — | — | 20·9 | — |
| 4·86 | 1·77 | 4·38 | 9·35 | 31·8 | 32·7 |
| 7·31 | — | — | 18·7 | 45·7 | 85·1 |

## BROWN PHOSPHORUS

If white phosphorus is heated above 600°C. and the vapour condensed at liquid nitrogen temperatures a coloured product is obtained. Condensation from 1000°C. or higher produces a dark-brown deposit which is insoluble in carbon disulphide, ethylene and propane. The material is also formed by irradiating white phosphorus at −190°C. with a quartz mercury vapour lamp.

Brown phosphorus is stable at −190°C. but begins to decompose irreversibly at −100°C. At room temperature the change is almost instantaneous. The decomposition always gives a mixture containing about 20% of red and 80% of white phosphorus.[239] At −43°C. to −88°C. the decomposition is first-order, the velocity constant being given by

$$\log_{10} k\,(\text{min.}^{-1}) = -\frac{738}{T} + 4{\cdot}49$$

## BLACK PHOSPHORUS

The methods of preparing dark-coloured products, described in the earlier literature as black phosphorus, have been summarized. Attention has been drawn to the fact these were impure forms of white phosphorus and that they should not be confused with the black allotrope first made by Bridgman under high pressure (Mellor, VIII, 747–8). A later observation[240] showed that white phosphorus could be converted into the black variety at room temperature and 35,000–40,000 atm. pressure, but there was some doubt as to whether this was the same as the product obtained at 12,000 atm. and 200°C. Similar results have been found when a pressure of 100,000 atm. is used,[241] the conversion being instantaneous under these conditions. The product, however, underwent a spontaneous reverse transformation to white phosphorus.

A more detailed study of the conversion of white to black phosphorus showed that there is an amorphous and a crystalline variety of the black allotrope. In the usual course of the formation of the crystalline form there is a slow transformation for 10 to 15 min. with slight decrease in volume. This is followed by a sudden transition during which the volume decreases extremely rapidly. The reaction goes instantaneously at any given pressure if the temperature is high enough. When there is no sudden decrease in volume within 15 min. an amorphous form is produced. The pressure–temperature relation is shown in Fig. 13. In region I only amorphous black phosphorus is formed. In region II there is an induction period for the reaction and in the third region crystalline black phosphorus is formed instantaneously. The amorphous form is not changed into the crystalline variety at 300°C. under 15,000 atm. pressure nor at 500°C. and 12,000 atm. pressure. The transformation of white into crystalline black phosphorus does not therefore proceed by formation of amorphous black phosphorus and subsequent change of this into the crystalline form. The transition from white to black phosphorus appears to occur because the heat of formation of the amorphous variety is sufficient to raise the temperature to a value high enough for the crystalline variety to be formed. For adiabatic conditions a 1% conversion of white to amorphous black phosphorus is sufficient to raise the temperature by 26°C.[242] More recent studies have shown that white phosphorus is very readily changed to the black form as the pressure is increased up to 100,000 atm.[243] No new modification of black phosphorus has been found at pressures up to 34,000 atm. and temperatures up to 600°C.[244] The m.p. rises with increased pressure and at 18,000 atm. black phosphorus melts at about 1000°C.[245] Further increase of pressure to 425,000 atm. does not alter the properties of black phosphorus.[246]

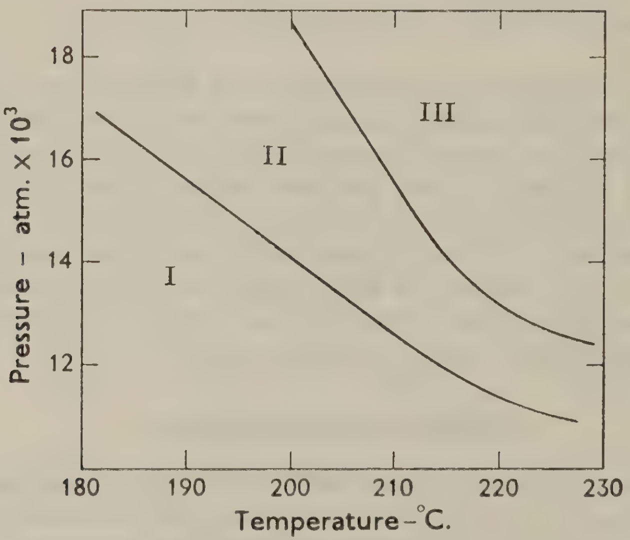

FIG. 13.—Pressure–temperature diagram for black phosphorus

Other observations have been reported[247] on the conversion of white phosphorus into the black modification at 100–200°C. and at pressures up to 48,500 kg./cm.$^2$ These indicate a longer conversion time and higher pressures for a given temperature than the results quoted above. From the data the temperatures and pressures above which white phosphorus cannot exist are given by the equation:

$$P\ (\text{kg./cm.}^2) = -379T + 193{,}273$$

where $T$ is the absolute temperature.[248] This gives a pressure of 82,000 atm. for a transition at 20°C. as compared with Bridgman's figure of 35,000 to 40,000 atm.[240]

**Refs. p. 143**

A low-pressure method of preparing black phosphorus has been described.[249, 252] According to this, white phosphorus is heated for 24–48 hr. at 250° to 600°C. in th presence of mercury which is then removed by extraction with molten lead at 300° to 400°C., to give a product containing about 1 at.-% of mercury. This is reduced to 0·4–0·5 at.-% by treatment with gold at 370° to 440°C. Pressures of 300 to 3,000 atm. assist the reaction.[250] Alkali metals, alkali metal phosphides, phosphine, ammonia, water and aliphatic tertiary amines are said to be catalysts.[251] *X*-Ray diagrams and physical properties show that the phosphorus made by this procedure is distinct from the very early forms of so-called black phosphorus. On the other hand it appears to oxidize in air more rapidly than red phosphorus and in the presence of moisture becomes coated with a viscous film of phosphoric acid.[250] Instead of mercury, molten bismuth has been used successfully as a recrystallizing solvent for black phosphorus.[253]

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## SECTION IV

# THE PHYSICAL PROPERTIES OF PHOSPHORUS

BY D. R. PECK

## NUCLEAR, ATOMIC AND MOLECULAR STRUCTURE

The atomic number of phosphorus is 15 and there is one stable isotope $^{31}_{15}$P. In addition, six radioactive isotopes have been reported up to 1958.[1] Table I gives a brief description of these isotopes. More detailed information is contained in the section on the radiochemistry of phosphorus.

*Table I.—The Isotopes of Phosphorus*

| Isotope | Half life | Type of decay | Physical at. wt. ($^{16}$O = 16·0000) | References |
|---|---|---|---|---|
| $^{28}$P | 0·28 sec.<br>0·29 sec.<br>0·27 sec. | $\beta^+$<br>$\gamma$ | 28·0012 | 1–5 |
| $^{29}$P | 4·45 sec.<br>4·60 sec. | $\beta^+$<br>$\gamma$ | 28·9910 | 1, 6–9 |
| $^{30}$P | 2·55 min.<br>2·52 min.<br>2·18 min. | $\beta^+$<br>$\gamma$ | 29·9881 | 1, 9–19 |
| $^{31}$P | Stable isotope | | 30·9836 | 1, 20–4 |
| $^{32}$P | 14·22 days<br>14·30 days<br>14·35 days<br>14·50 days<br>14·07 days<br>14·60 days | $\beta^-$<br>(no $\gamma$) | 31·9842 | 1, 9, 18, 23, 25–41 |
| $^{33}$P | 24·4 days<br>24·8 days<br>25·0 days | $\beta^-$<br>(no $\gamma$) | 32·9822 | 1, 9, 23, 34, 37, 42, 43 |
| $^{34}$P | 12·4 sec.<br>12·7 sec. | $\beta^-$<br>$\gamma$ | 33·9826 | 1, 9, 44–7 |

The atomic weights in the above table are given in atomic mass units (1 A.M.U. $= 1{\cdot}661 \times 10^{-24}$ g.) based on the $^{16}$O oxygen isotope with an atomic weight of exactly 16. They can be converted to the chemical scale by dividing by 1·000275. It should be noted that the chemical and physical atomic weight scales were replaced in 1960 by a single scale based on the $^{12}$C carbon isotope with an atomic weight of 12·0000. This is discussed in more detail on page 217.

A complete list of nuclidic masses on the $^{12}$C scale is given in reference 48 from which the data in Table II are taken.

The nucleus of the stable isotope $^{31}_{15}P$ has been described[49, 50] as consisting of 15 protons and 16 neutrons: the forces between these are due to exchange processes which involve the transformation of neutrons into protons and *vice versa*. The neutrino and several types of mesons are also thought to be involved in this transformation.[51]

Evidence has been reported[52] which leads to the hypothesis that the nucleus of an atom consists of closed shells of protons and neutrons.[53–4] On this basis the configuration of the nucleus of the phosphorus atom is given as $1s^2 2p^6 3d^6 2s^1$.[55–6]

*Table II.—Relative Nuclidic Masses of Phosphorus Isotopes*

| Isotope | Nuclidic mass | |
|---|---|---|
| | $^{12}C = 12{\cdot}0000$ | $^{16}O = 16{\cdot}0000$ |
| $^{28}P$ | $27{\cdot}99174 \pm 3{\cdot}2 \times 10^{-4}$ | 28·00064 |
| $^{29}P$ | $28{\cdot}981816 \pm 0{\cdot}1 \times 10^{-4}$ | 28·99103 |
| $^{30}P$ | $29{\cdot}97832 \pm 0{\cdot}1 \times 10^{-4}$ | 29·98785 |
| $^{31}P$ | $30{\cdot}973763 \pm 0{\cdot}02 \times 10^{-4}$ | 30·98361 |
| $^{32}P$ | $31{\cdot}973908 \pm 0{\cdot}02 \times 10^{-4}$ | 31·98407 |
| $^{33}P$ | $32{\cdot}971728 \pm 0{\cdot}02 \times 10^{-4}$ | 32·98221 |
| $^{34}P$ | $33{\cdot}973340 \pm 2{\cdot}1 \times 10^{-4}$ | 33·98414 |

An analysis of the emission spectrum of diatomic phosphorus vapour shows that the nuclear spin is $\frac{1}{2}\hbar$.[57] The nuclear magnetic dipole moment has been variously reported to be +1·1317[58–60] and 1·13165[61] nuclear magnetons, the most recent value being 1·1305.[1] The nuclear quadrupole moment is zero, indicating a spherically symmetrical charge distribution in the nucleus. The diameter of the nucleus is about $10^{-12}$ cm. and the atomic diameter about $2 \times 10^{-7}$ cm.

The neutral state of the stable isotope of phosphorus has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^3$, the ground term being $4s_{3/2}$. The ionization potentials, in electron volts (1 e.v. = 23·053 kcal. mole$^{-1}$) for successive ionization stages, are given in Table III.[62] As will be seen from this Table, the energy required to form $P^{3+}$ and $P^{5+}$ ions is 695 and 1498 kcal. mole$^{-1}$ respectively. These energies are much higher than the heats of most chemical reactions carried out at temperatures below 1000°C. and indicate that in most of the stable compounds of phosphorus there is little or no charge on the phosphorus atom.

*Table III.—Ionization Potentials of Phosphorus*[62]

| Initial state | Ionization potential e.v. | Initial state | Ionization potential e.v. |
|---|---|---|---|
| P(I) $3p^3\ {}^4S_{3/2}$ | 11·0 | P(VIII) $2p^4\ {}^3P_2$ | 309·26 |
| P(II) $3p^2\ {}^3P_0$ | 19·65 | P(IX) $2p^3\ {}^4S_{3/2}$ | 372·62 |
| P(III) $3p\ {}^2P_{1/2}$ | 30·16 | P(X) $2p^2\ {}^3P_0$ | 425·46 |
| P(IV) $3s^2\ {}^1S_0$ | 51·36 | P(XI) $2p\ {}^2P_{1/2}$ | 479·4 |
| P(V) $3s\ {}^2S_{1/2}$ | 65·01 | P(XII) $2s^2\ {}^1S_0$ | 560·3 |
| P(VI) $2p^6\ {}^1S_0$ | 220·41 | P(XIII) $2s\ {}^2S_{1/2}$ | 611·45 |
| P(VII) $2p^5\ {}^2P_{3/2}$ | 263·31 | | |

At temperatures below 800°C. electron diffraction data[63] show that phosphorus vapour is composed of tetratomic molecules, in which the phosphorus atoms are situated at the corners of regular tetrahedra. The P–P distance is 2·21 ± 0·02 Å. and the moments of inertia are $I_A = I_B = I_C = 251 \times 10^{-40}$ g.cm.$^2$ Since the bond angle in the $P_4$ molecule is 60° as compared with 90° for an unstrained P–P–P linkage, it has been calculated that there is a strain energy of 22·8 kcal. mole$^{-1}$ in the molecule.[64] This is discussed in more detail in the section on valency (page 153).

The tetrahedral structure has been shown to persist in liquid and solid white phosphorus. *X*-Ray diffraction shows that liquid phosphorus is composed of $P_4$ molecules which are tetrahedral with a P–P distance of 2·25 A.[65] Infra-red[66–7] and Raman[68–9] spectra show only small frequency changes in passing from the solid through liquid to the vapour phase of white phosphorus. Interpretation of the vibrational spectrum is consistent with a tetrahedral structure of $T_d$ symmetry.[67, 70] In the ordinary or α-form of solid white phosphorus the $P_4$ tetrahedra are free to rotate.

At temperatures above 800°C. phosphorus is dissociated into $P_2$ molecules. The emission[57, 71–2] and ultra-violet[73–5] absorption spectra have been studied and from the emission spectrum the vibrational energy levels are represented by the equation[76]

$$E_v/hc = 780{\cdot}43(v+\tfrac{1}{2}) - 2{\cdot}804(v+\tfrac{1}{2})^2 \text{ cm.}^{-1}$$

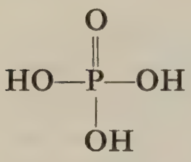
The original values of $90{\cdot}47 \times 10^{-40}$ g. cm.$^2$ for the moment of inertia and 1·88 A. for the internuclear distance were calculated[77] from the emission spectrum data.[78] More recent values, considered to be more accurate, are $92{\cdot}36 \times 10^{-40}$ g. cm.$^2$ and 1·895 A. respectively.[74] The spectrum of the $P_2^+$ molecule has been analysed. This shows two band systems which are attributed to the $P_2^+$ molecule. One of these, which in its lower region probably corresponds to the ground state of the $P_2{}^+$ molecule, is a $^2\Pi$–$^2\Pi$ band system at a wave-length of 3400–3850 A. The other one is a $^2\Sigma$–$^2\Sigma$ system lying in the region 3900–4400 A.[79]

Dissociation of diatomic phosphorus into phosphorus atoms of ground state $^4S_{3/2}$ and nuclear spin $\frac{1}{2}\hbar$ requires a dissociation energy of 5·033 electron volts (116 kcal. mole$^{-1}$) at absolute zero.[80] Spectroscopic calculations[77] show that at 1500°C. the amount of monatomic phosphorus in the vapour is less than 0·01% (see page 201, Table XLVII). Calculations[484] based on the spin polarization concept predict a negative sign for the magnetic hyperfine constant of the $^4S$ ground state of $^{31}P$, which is at variance with the positive value obtained experimentally.[485–6]

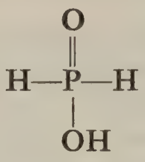
## VALENCY AND CHEMICAL BONDING OF PHOSPHORUS

In common with the other elements of the second short period of the Periodic System, phosphorus can have a normal valence V as well as one of V − 8. The oxidation state is +5 when five electrons are removed from the outer or M-shell and −3 when three electrons are added to it. It was even suggested that white phosphorus should be formulated with a phosphide structure $(P^{3+})(P^-)$. This was claimed to explain a number of reactions, such as the formation of phosphine and hypophosphite from phosphorus and caustic alkalis and the reaction of phosphorus with copper sulphate to give copper, copper phosphide and phosphoric acid.[81] However, this view implies that phosphorus ions exist in phosphorus compounds; i.e. that the phosphorus carries an electrical charge which is not neutralized by opposite charges on atoms to which it is bonded. Although both positive and negative ions have been produced under exceptional conditions, for example when phosphorus vapour is subjected to the action of an electric discharge,[82] it would appear that ionized phosphorus is not common under normal conditions. The investigations of Van Wazer and co-workers[50, 83] have provided substantial evidence in favour of the view that phosphorus is covalently bonded in the majority of its compounds. Nuclear magnetic resonance studies show that the picture of sodium phosphates made up of close-packed $P^{5+}$, $Na^+$ and $O^{2-}$ ions, with alternation of positive and negative charges, is erroneous. The spin-spin splitting observed in the N.M.R. spectra of phosphorus compounds is more closely in agreement with a structure of covalently-bonded phosphorus and oxygen atoms making up phosphate molecule-anions. The negative charges of these are then balanced by counter ions, such as $Na^+$, some of which may be closely associated with the oxygen atoms of the molecule-anion. For example, N.M.R. measurements show that in the tripoly- and tetrapolyphosphate anions the P–O–P linkages are essentially covalent. The data also indicate that the postulated $P^{5+}$ ion does not exist in phosphates.[83] In many molecules of which the structure has been determined by *X*-ray methods, phosphorus is found to be joined to the other atoms by covalent bonds. More detailed information is given in Section XXXIV. It has been shown, for example, that $P_4O_{12}^{4-}$ ions are present in crystalline aluminium metaphosphate[84] and in ammonium tetrametaphosphate.[85] In the latter the ammonium ions form hydrogen bonds with the oxygen atoms of the tetrametaphosphate anion.[86] Similar structures have been found for phosphoric acid[87] and phosphorus oxides.[88] Hartree–Fock–Slater atomic scattering factors for phosphorus in a number of valence hybrid states have been presented.[482–3]

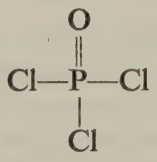
According to classical ideas of valency, phosphorus is regarded as being either tervalent or pentavalent. This has given rise to a notation in which compounds containing phosphorus joined to four other atoms are represented with a double bond as shown below:



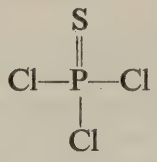
$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}OH}$



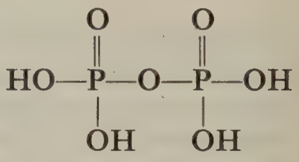
$\mathrm{H{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}H}$



$\mathrm{Cl{-}\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{P}}{-}Cl}$



$\mathrm{Cl{-}\overset{\overset{S}{\|}}{\underset{\underset{Cl}{|}}{P}}{-}Cl}$



$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}OH}$

As an alternative, the double bond is often replaced by an arrow to indicate a co-ordinate linkage or a dative or semi-polar bond in which the bonding is formed from two electrons both of which are contributed by the phosphorus atom to the oxygen or to the sulphur atom. These ideas, however, suggest that in the orthophosphate ion, for example, one of the four oxygen atoms would differ from the other three. There is no physical evidence for this; physical data indicate that all four oxygen atoms are equivalent.

Phosphorus in its compounds can be linked with 1, 3, 4, 5 or 6 other atoms, the most common co-ordination numbers being 3 and 4. Compounds of co-ordination number 1 are very unstable under normal conditions, but have been identified in band spectra. Those with co-ordination number 3 are reasonably stable, but act as electron donors. In so doing the phosphorus increases its co-ordination number to 4, in which state it is the most stable. Compounds in which phosphorus is joined to five or six atoms are very reactive and only a few are known, e.g. $P(C_6H_5)_5$, $PCl_2F_3$, $PBr_2F_3$, $PBr_5$ and the anions $PF_6^-$ and $PCl_6^-$.[89]

The observed interatomic distances of 3-co-ordinate phosphorus compounds agree with values calculated from covalent radii[90] or from atomic radii and bond energies.[91] For single and 4-co-ordinate compounds the observed distances are usually shorter than the calculated values[91–2] and this has been attributed to $\pi$-bonding.[93] The molecular orbital theory postulates that single bonds are formed by collinear overlapping of atomic orbitals. These bonds, which are symmetrical and known as $\sigma$ bonds, occur when an *s*-orbital combines with any other kind of orbital, and when *p*- and *d*-orbitals combine end to end. When *p*- and *d*-orbitals overlap sideways or *d*-orbitals combine in a similar manner, $\pi$-bonds are said to be formed. In applying this to phosphorus compounds, Van Wazer[89] finds that for diatomic molecules, in which the bonding occurs mainly through *p*-orbital electrons, there are between one and two $\pi$-bonds per $\sigma$-bond. In 3-co-ordinated compounds the bonding has primarily a $p^3$-orbital character and here $\pi$-bonding is slight or absent. The 4-co-ordinated phosphorus has $sp^3$-bonding characteristics and it is found that in these compounds there are three or four $\sigma$-bonds to every $\pi$-bond. When the phosphorus is linked to five or six other atoms the *d*-orbitals, five in number, which have energy levels not greatly above the 3*s*- and 3*p*-orbitals, are involved. This gives rise to $sp^3d$ and $sp^3d^2$ hybridization respectively, and in such compounds virtually no $\pi$-bonding is observed. Because the energy of promotion of an electron into a *d*-orbital is large, these higher valencies are developed only when the energy of formation is great, i.e. when phosphorus is combined with fluorine or oxygen.[94]

These generalizations do not give a complete explanation of all the observed bonding phenomena in phosphorus compounds. For example, the amount of $\pi$-bonding as determined from observed bond lengths in rubidium metaphosphate,[95] phosphorus pentoxide,[88] phosphorus sulphoxide[96] and in phosphorus oxyhalides, thiohalides[97] and mixed halides[98] is between 0·8 and 1·5 $\pi$-bonds per $\sigma$-bond for the P–O and P–S linkages. 4-Co-ordinated phosphorus compounds containing phenyl groups show very little $\pi$-bonding for such phosphorus atoms.[99–101] On the other hand, quantum mechanics indicates that $\pi$-bonding should be found in 4-co-ordinated phosphorus compounds and should be absent in 3-, 5- and 6-co-ordinated ones.[102] Nuclear magnetic resonance data from phosphorus compounds can also be explained on the basis of changes in the hybridization and $\pi$-bond character of the phosphorus atom.[103] Resonance shifts between similar or homologous phosphorus compounds have been explained by considering changes in the relative importance of their ionic and double-bonded electronic structures.[104]

Solid,[105] liquid[65, 68–9] and gaseous[63, 66] phosphorus all contain the tetra-atomic $P_4$ molecules in which the phosphorus atoms are arranged in tetrahedra. The angles between the bonds are 60° and the bonding has predominantly $p^3$-orbital characteristics.[106] Because the three $p$-orbitals are at right angles to one another, the bond angle in the P–P–P linkage should be 90°. It has been suggested[107] that this could be explained by supposing that the phosphorus atoms are bonded by $pd^2$ hybrid orbitals. Although this gives a bond angle of nearly 60°, spectroscopic data show that the promotion of a $3p$-electron to a $3d$-orbital requires about 194 kcal. mole$^{-1}$. To form three $pd^2$ bonds, two electrons have to be promoted, corresponding to an energy of 388 kcal. for the $P_4$ molecule. The energy requirement is considerably less if the molecule is assumed to contain bent or strained bonds. However, a more recent treatment predicts that strong $\pi$-bonds are present in the molecule, and their presence leads to a resonance which in turn makes it unnecessary to postulate 'bent bonds', and vitiates the concept of 'strain energy' in $P_4$. A calculation of the electronic spectrum of $P_4$ assuming a pure $3p$ basis was in adequate agreement with the observed spectrum.[488] The P–P bond energy for an angle of 60° in the $P_4$ molecule has been estimated to be 44 kcal. mole$^{-1}$,[108] increasing to 47·5 kcal. mole$^{-1}$ for a normal bond, thus giving a strain energy of 3·5 kcal. per P–P bond. By assuming that the bonds are formed by pure $p^3$-orbitals, the strain energy has been calculated to be 7·1 kcal. for every P–P bond.[109] The bonding has also been described in terms of *pd* hybridization[110] and this has been extended to *spd* hybrid bond orbitals involving a bond angle of 73°.[111] The latter hybridization has been adapted for a bond angle of 60°.[112] In black phosphorus and in the phosphorus trihalides the P–P bond angle varies between 99° and 102°. By assuming that the normal bond angle is 101° and considering the bonds to be *spd* hybrids, the strain energy has been calculated[64] to be 3·8 kcal. per P–P bond or 22·8 kcal. mole$^{-1}$ per $P_4$ molecule. The character of this type of bonding is largely that of a $p$-orbital, the contribution of the $3s$-orbital being about 0·4% and that of the $3d$-orbital about 2·2%. The bond angles,[113] valency[114] and bond characteristics[115] in phosphorus compounds have been discussed by a number of authors. Molecular orbital calculations have been reported for pentavalent phosphorus compounds. From these it appears that a free-atom $3d$ atomic orbital is too diffuse to give a strong bond by itself. There is, however, evidence that some $d$-hybridization occurs.[116] The effect of the availability of $3d$-orbitals on the mechanism and the products of the general reactions of phosphorus has been discussed in some detail.[117] Various empirical relations have been proposed connecting bond length with potential energy,[118] bond multiplicity,[119] internuclear distances in crystals[120] and the ionic radii of positive and negative ions.[121] These apply to phosphorus with various degrees of accuracy. A more accurate expression is

$$R = R_1\left[\frac{2}{3}+\frac{1}{3}\left(\frac{n-1}{n+1}\right)^{p/2}\right]$$

where $R$ is the covalent bond distance, $R_1$ the length of a single bond, $n$ is the principal quantum number of the valence electrons and $p$, the bond order, is 0 for a single bond, 1 for a double bond and 2 for a triple bond.[122]

## ATOMIC RADII OF PHOSPHORUS

Various atomic or structural radii have been reported for phosphorus. The normal covalent radius and the tetrahedral covalent radius have the same value, 1·10 A. for a single bond,[123] obtained by dividing the P–P bond distance by two.[63] This value has been used to calculate bond distances in phosphorus compounds, but in most instances a correction is necessary to allow for the partial ionic character of bonds formed between phosphorus and atoms other than itself. An approximation for this correction is based on the difference ($X_A \sim X_B$) of the Pauling electronegativities of the atoms concerned (see page 183). The bond length is then given by the expression

$$r_{AB} = r_A + r_B - 0{\cdot}09(X_A \sim X_B)$$

where $r_A$ and $r_B$ are the covalent radii of the atoms.[87]

This method of calculation gives bond lengths which are longer for P–O and P–F linkages by 0·1–0·2 A. than observed values.[124] Better agreement is found by using the relationship

$$r_{AB} = R_A + R_B - \tfrac{1}{2}\log_{10} D_{AB}$$

where $D_{AB}$ is the bond energy in kcal. mole$^{-1}$ and $R$ is the constant energy covalent radius. Values of $R$ have been computed[91] by considering the radius of an atom in an environment where the repulsion energy is constant. For phosphorus this radius is 1·53 A. Using this radius and the above expression, P–O and P–F bond distances can be estimated to within 0·05 A. of the values obtained by electron diffraction.[125–6]

An atomic radius of 1·28 A. has been calculated for a 12-co-ordinate phosphorus atom in which the atoms are joined by electron-pair bonds and the lattice is body-centred cubic.[127] A value of 1·65 A. has been given for a non-bonded electronegative phosphorus atom surrounded by twelve equidistant atoms.[128] The atomic radius has been estimated to be 1·70 A. from compressibility and thermal expansion data (see page 172).

The above data, together with values for other radii, are summarized in Table IV.

*Table IV.—Covalent, Atomic and Crystal Radii of Phosphorus*

| Type of radius | Radius, A. | Ref. |
|---|---|---|
| Normal covalent | 1·10 | 123 |
| Tetrahedral covalent | 1·10 | 123 |
| Constant energy covalent | 1·53 | 91 |
| 12-Co-ordinated metallic | 1·28 | 127 |
| Double bond covalent | 1·00 | 123 |
| Triple bond covalent | 0·93 | 123 |
| Non-bonded or Van der Waals | 1·90 | 123 |
| Univalent ionic for $P^{5+}$ | 0·59 | 129 |
| Univalent ionic for $P^{3-}$ | 2·79 | 129 |
| Crystal for $P^{5+}$ | 0·34 | 129 |
| Crystal for $P^{3-}$ | 2·12 | 129 |
| 12-Co-ordinated covalent | 1·65 | 128 |
| Atomic (calculated) | 1·70 | 130 |

The univalent ionic radius is hypothetical and refers to the value which the radius would have if phosphorus behaved as a univalent ion. It should be noted that although a value has been reported for the crystal radius of the pentavalent phosphorus ion, it is unlikely that this ion exists in phosphorus compounds.

Other data useful for estimating bond lengths are listed on page 213, Table LXII.

## THE ALLOTROPES OF PHOSPHORUS

Solid phosphorus exists in more polymorphic forms than almost any other element. Most of the allotropes have more than one variety. For example, there are two crystalline forms of white phosphorus, an amorphous and crystalline black phosphorus and several varieties of red phosphorus. The phase relations of the main forms have previously been discussed (Mellor, VIII, 752). The known allotropes are shown in Table V.

*Table V.—Allotropic Modifications of Phosphorus*

| Allotrope | Crystal structure | Density (g. c.c.$^{-1}$) | m.p. (°C.) | Heat of sublimation (kcal. mole$^{-1}$) |
|---|---|---|---|---|
| α-white | Cubic | 1·828 | 44·1 | 13·4 |
| β-white | Orthorhombic | 1·88 | — | — |
| Red I | Amorphous | 2·16 | — | 19·7 |
| Red II | Probably hexagonal | 2·31 | — | 24 |
| Red III | Probably hexagonal | 2·31 | — | — |
| Red IV | Tetragonal | 2·31 | — | 28 |
| Red V | Triclinic | 2·31 | 590 | 28·8 |
| Red VI | ? | ? | ? | ? |
| Black I | Amorphous | 2·25 | — | — |
| Black II | Orthorhombic | 2·69 | — | 38·7 |
| Vitreous | ? | 2·26 | — | — |
| Brown | ? | ? | Decomp. | Decomp. |

### α-White Phosphorus

This is the common form of the element and is always obtained when phosphorus vapour is condensed to a liquid and this is allowed to solidify. It normally has a yellowish coloration, but can be formed as white crystals by cooling a saturated solution of phosphorus in benzene. Transparent crystals have been obtained from a benzene solution at 200°C. and 60–70 atmospheres pressure. White phosphorus is also produced when the red form is sublimed in a vacuum (10 mm. pressure or less) at temperatures of 500°C. and over.[131]

The α-form crystallizes in the cubic system and the lattice constant is $a = 18{\cdot}51$ A.[105] The value $a = 7{\cdot}17$ A. reported earlier appears to be in error.[132] The molecular unit in the solid is $P_4$ and the unit cell contains 56 units.

### β-White Phosphorus

This variety is formed by cooling α-white phosphorus to below the transition temperature of −76·9°C. at ordinary atmospheric pressure. The effect of pressure on the transition temperature is shown in Fig. 1.[133] β-White phosphorus is doubly refractive[134] whereas the high temperature form is isotropic.[135–6]

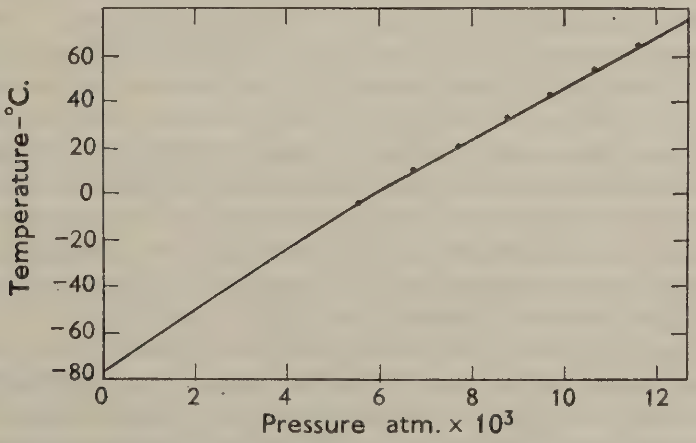


FIG. 1.—Effect of pressure on the transition temperature of α- to β-phosphorus

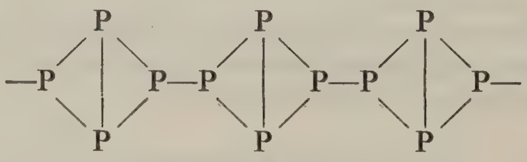
The instability of white phosphorus has been attributed to strain in the molecule caused by the 40° distortion of the valence angles.[137]

## Red Phosphorus

The structure, properties and forms of red phosphorus have been the subject of many conflicting reports in the literature. It has been classed as amorphous (Mellor, VIII, 745), cubic,[138] monoclinic,[139] hexagonal and triclinic.[140] The colour has been described as red,[141–2] scarlet,[136] purple,[144] violet,[145] ruby[144] and metallic.[146] It has been considered to be a mixture of the black and purple forms,[147] a solid solution of the ruby and purple varieties,[148] an equilibrium state between white and violet,[149] and a solid solution of several varieties of red phosphorus (Mellor, VIII, 752). It has also been described as a polymer of white phosphorus in which terminal groups such as hydroxyl, or bromine or iodine atoms[150] are present, and a combination of minute particles of the violet allotrope on which white phosphorus is adsorbed.[142]

It is evident that the method of preparation and subsequent treatment of red phosphorus have a marked influence on its structure and properties. Significant differences have been found in the thermochemical properties and vapour pressure of red phosphorus made at different temperatures.[146] Varieties prepared by heating white phosphorus in the presence of catalysts usually have an ill-defined crystal structure, a density of between 2·10 and 2·32, and vary in colour from red to violet.[142] Large crystals of red phosphorus are generally purple in colour, but the finely divided material can be scarlet.[151]

The hypothesis that some forms of red phosphorus may contain foreign atoms is supported by a number of observations. It is known that in the conversion of white to amorphous red phosphorus the latter takes up catalysts such as iodine or sulphur.[152] This reaction may be regarded as a type of polymerization, in that the tetrahedral $P_4$ unit of white phosphorus is converted into a more complex structure. For example, it has been suggested[64] that the $P_4$ molecule is opened by the rupture of a single P–P bond, leading to the formation of long chains of bonded atoms arranged in a manner similar to the following:



In such an arrangement, catalyst atoms could act as terminal groups or might give rise to a cross-linked network of chains. If white phosphorus is heated in the presence of water, yellow or yellowish brown products are obtained which contain 15–44 atomic-% of hydrogen. In the presence of light and moisture, purple materials are formed. These contain 10% of phosphorus oxides and water combined as hydrogen atoms and hydroxyl groups. The scarlet phosphorus of Schenck,[143] which is prepared by heating white phosphorus with phosphorus tribromide, is a polymer containing 10–30 at.-% of bromine, i.e. one out of 7–27 of the phosphorus valency bonds is joined to a bromine atom. Washing this product with water removes the bromine atoms and replaces them with hydroxyl groups.[153] Orange-coloured products are also formed when pentaerythritol tetrabromide is prepared by refluxing 1 mole of pentaerythritol with 2 moles of phosphorus tribromide at up to 175°C.[153a] The coloured material contains bromine, but because it was treated with water at an intermediate stage in the preparation, it is possible that it may also contain some of the lower oxidation product $(P_4(OH))_n$ (see page 245).[153b]

If organic halides are used as solvent the organic radical is strongly attached to the phosphorus and cannot be removed by boiling water. Oxidation of the product with nitric acid gives alkyl or aryl phosphinic acids (Van Wazer, reference 50, page 115). Irradiation of white phosphorus in a solvent, e.g. carbon disulphide, yields an amorphous red phosphorus containing impurities derived from the solvent.[150, 153]

Similar results have been observed when the conversion of white to red phosphorus in diphenylmethane is catalyzed by tributylamine.[154]

Commercial red phosphorus is usually amorphous or micro-crystalline. The amorphous form is obtained in laboratory preparations carried out below 350°C. or by depositing red phosphorus from the vapour which has been in contact with a hot tungsten filament at 200° to 425°C.[140] *X*-Ray studies show that the radial distribution curve has peaks at 2·29 and 3·50 A., from which it is inferred that the P–P–P bond angle is about 99°.[65, 475] The effect of heat on amorphous red phosphorus has been investigated by *X*-ray and differential thermal analysis procedures.[140] Exothermic peaks corresponding to about 200, 70 and 50 g.-cal./g. atom respectively are found at 460°, 520° and 540°C. The initial material was that designated as red phosphorus-I in Table V and was prepared by heating white phosphorus for 6–8 hr. at 280°C. in an inert atmosphere. The density as determined by a nitrogen gas densitometer was 2·16 g./c.c. It should be noted that this is lower than the density of 2·32–2·34 obtained for commercial amorphous phosphorus. The difference is most probably due to the higher temperatures (400° to 450°C.) used in the final stages of the manufacture of the commercial product. The differential thermal analysis peak at 460°C. corresponds to the transformation of red phosphorus-I into form II. This is followed by transformation into form III and form IV at 520° and 540°C., respectively. Form II and form III are poorly-crystallized materials and may be identical. They may also be identical with form IV which is tetragonal.[478] On the other hand, microscopical examination does indicate that there are both hexagonal and tetragonal varieties of red phosphorus. Form IV is birefringent and well-formed crystals have been obtained by slow condensation of phosphorus vapour at 425°C. and 1 atm. pressure, or at 20 atm. by heating to 535°C. and condensing on a surface at 500° to 510°C.[155] A micro-crystalline variety has been obtained by crystallization at 550°C.[139]

The best defined variety of red phosphorus is form V, which is triclinic. Differential thermal analysis shows no peak corresponding to the transition from form IV to form V. The material has been prepared by condensing phosphorus vapour at 550°C. on to a surface at 545°C. over a period of 30 days, or by heating amorphous red phosphorus at 550°C. for 6–30 days. *X*-Ray patterns of phosphorus-V are similar to those given by Hittorf's metallic or violet phosphorus. The latter was obtained[156] by heating phosphorus with lead at 500° to 600°C. in a sealed tube, then cooling and removing the lead by dissolving in dilute nitric acid. Similar patterns are given by material crystallized from lead at 525° to 590°C. or from bismuth at 570° to 580°C.[138] in sealed tubes. However, a detailed crystallographic study of Hittorf's violet phosphorus has shown that it crystallizes in the monoclinic system with space group $P2/c$, $a = 9{\cdot}21$, $b = 9{\cdot}15$, $c = 22{\cdot}59$ A., $\beta = 106{\cdot}1°$, and 84 atoms in the unit cell. The structure is based on two units, a $P_8$ group and a $P_9$ group, which are linked, each through two further phosphorus atoms, to form infinite tube-like structures of pentagonal cross section (Fig. 2). The tubes are packed parallel to one another in layers, pairs of layers being arranged roughly at right angles to one another.[487]

Red phosphorus-VI was obtained by heating white phosphorus at 300°C. and a pressure of 8000 atm.[157] It is deep red in colour and differs in appearance and in its *X*-ray pattern from other forms of red phosphorus. The material does not appear to have been examined in any detail.

Vitreous phosphorus has recently been reported to be formed by heating white phosphorus to above 250°C. under a pressure of 7000 atm. No sudden volume change, such as that which occurs in the formation of black phosphorus, was observed during this operation. The same material was obtained by heating white phosphorus with mercury in a sealed tube for 4 days at 380°C. (not above); the mercury was then extracted with molten lead or gold. Red phosphorus was not changed to the vitreous form by either of these procedures. The material is amorphous and has *d* 2·26. Its resistivity is above 1000 ohm-cm. at room temperature, increasing to a kilo-megohm-cm. in liquid nitrogen. Vitreous phosphorus is stable for an indefinite period in warm, moist air, but is oxidized slowly by nitric acid and rapidly by aqueous bromine. It sparks like flint when sawn or struck and may ignite. When heated in a sealed tube it is converted to red phosphorus in 4 days at 400°C. Under the same conditions in the presence of mercury it gives amorphous black phosphorus. On subliming in a vacuum, white phosphorus is formed. The various transformations which are possible between the different forms of phosphorus are shown diagrammatically in Fig. 3. It should be noted that there are no records of any changes from the black or red modifications of phosphorus to the vitreous form.[158]

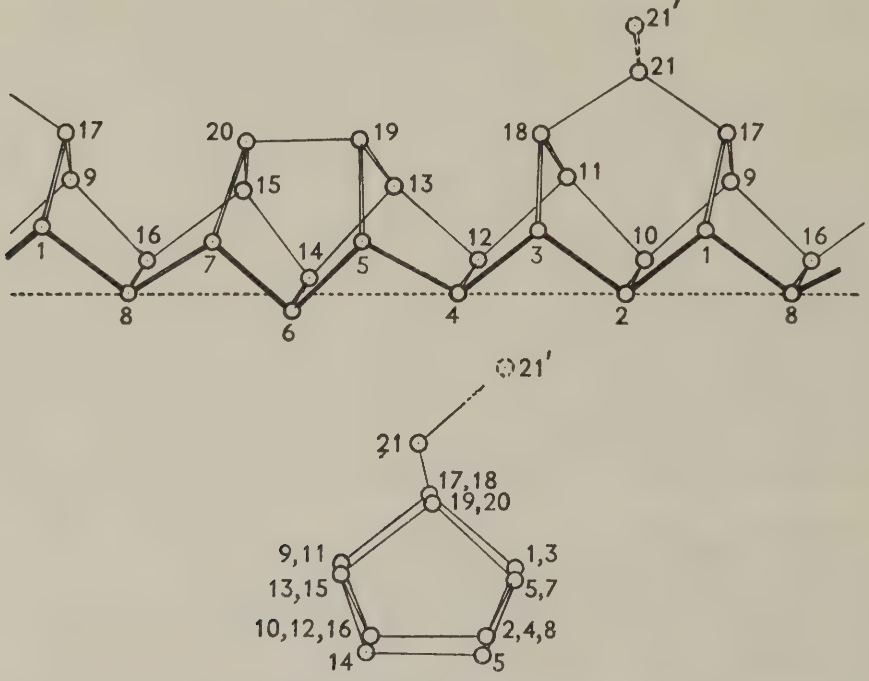


FIG. 2.—Section of a 'tube' of violet phosphorus. Above: parallel perspective. Below: projection parallel to the tube axis (end view)

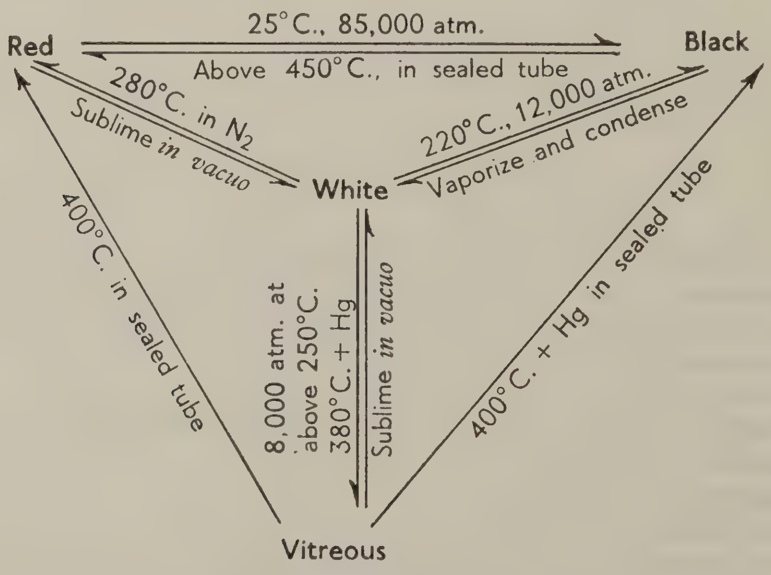


FIG. 3.—Transformations between allotropes of phosphorus

Approximate equations for the sublimation pressure of four modifications of phosphorus described above have been obtained.[155] These are given in Table VI.

Of the above equations, that for red phosphorus-V is considered to be the most accurate and reliable. The data for forms I and II may be subject to some error due to changes which the materials undergo when heated above 400°C.

Three other forms of red phosphorus have been reported. One of these is a cubic form made by heating ordinary red phosphorus at 600°C.[159] A reversible transition of red phosphorus to a new modification is said to occur at 600°C. under a pressure of about 40,000 atm.[160, 161] A new form of red phosphorus has been observed when yellow phosphorus is irradiated for 30 hr. with copper *X*-radiation (35 kv., 5 ma.). The yield was 4·5%.[136] There does not appear to be sufficient evidence to decide whether any of these forms are distinct from those described above. In later experiments, in which samples of red phosphorus were prepared at temperatures from 300° to 610°C., only two allotropic forms of red phosphorus were observed, corresponding to forms IV and V described above. They were well crystallized, and exhibited completely different *X*-ray diffraction and fluorescence spectra, one set associated with samples heated at temperatures greater than 426°C., and the other with samples heated to less than 420°C. Other *X*-ray diffraction patterns observed, which resembled those of forms I, II and III, were claimed to be associated with the growth of crystallites with poorly diffracting planes of less than 50 A. to well-developed crystallites, and were a regular function of the temperature at which the samples were prepared.[478]

*Table VI.—Sublimation Pressure Equations and Heats of Sublimation of Red Phosphorus*[155]

| Form | Equation ($p$ atm., $T$°K.) | Temp. (°C.) | Heat of sublimation (kcal. mole$^{-1}$) |
|---|---|---|---|
| I | $\log p = -4296/T + 6{\cdot}404$ | 320–500 | 19·7 |
| II | $\log p = -5250/T + 7{\cdot}61$ | 310–500 | 24 |
| IV | $\log p = -6070/T + 8{\cdot}67$ | 380–560 | 28 |
| V | $\log p = -6298/T + 8{\cdot}944$ | 320–510 | 28·8 |

Brown phosphorus, which may have some relation to the red variety, has been described in the section on the preparation of phosphorus (p. 141).

## Black Phosphorus

Reference has been made (page 142) to the two forms of black phosphorus, and to some of their properties, in a previous section. Crystalline black phosphorus is orthorhombic, with lattice constants of $a = 3{\cdot}3136$, $b = 10{\cdot}478$, $c = 4{\cdot}3763$ A.[481] There are eight phosphorus atoms in the unit cell, and the density is 2·70.[157, 162] The crystal is made up of double layers in which each phosphorus atom is bonded with three neighbours at distances of 2·244, 2·224, 2·224 A. Two of the bonds are in the plane of a layer, with a bond angle of 96·34°. The third is between the layers, with a bond angle of 102·09°. The nearest approach of atoms in adjacent layers is 3·59 A.[481] These data are a refinement of earlier measurements.[157, 152] The arrangement of the atoms is shown in Fig. 4.

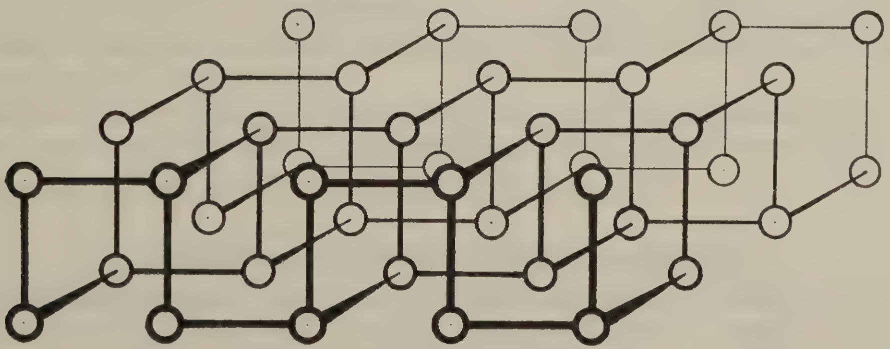


FIG. 4.—Structure of black phosphorus

Black phosphorus is completely stable in air and can be cut and machined without igniting, but burns with difficulty on being lighted. It is flaky and similar in appearance to graphite, though it has no free electrons which can move in the direction of the cleavage planes of the crystal (Van Wazer, reference 50, page 123). On heating at 550°C. it is converted to violet phosphorus. It can be crystallized from solutions of phosphorus in liquid bismuth.[481]

Amorphous black phosphorus, which is prepared by heating white phosphorus under high pressures but at temperatures lower than those required for the formation of the crystalline variety, has $d$ 2·25 g./c.c. $X$-Ray data[163] show that each phosphorus atom is bonded to three neighbours at a distance of 2·27 A. The next nearest atoms are at a distance of 3·34 A. The structure contains no simple $P_4$ molecules and is similar to that of red phosphorus.[65] The most probable atomic arrangement is a puckered network for which the average bond angle is 95·6°. The amorphous form appears to be less stable than the crystalline variety because on prolonged heating at 125°C. it is transformed into violet phosphorus.[164]

Black phosphorus forms mixed crystals with arsenic. For a composition of 53–74 atom-% of arsenic it is sufficient to cool a melt of the required composition. For crystals containing 43–53 atom-% of arsenic the melt has to be heated for several days at 600°C. and for 0–43 atom-% it is necessary to use mercury as a catalyst.[165]

Resonance bonding of $p$-orbital electrons is said to occur in black phosphorus.[166] The characteristic crystal lattice has been explained in terms of the distortion of a symmetrical crystal lattice by unsymmetrical resonance bonds arising from hybridized atomic orbitals.[167] It has also been suggested that the polymorphic forms of phosphorus are chemical isomers, according to which white phosphorus is constituted as $P_4$, red as $(P_2)_n$ and black as $P_8$ or $(P_2)_4$.[168]

*Table VII.—The Best-known Modifications of Phosphorus*

| Modification | Specific gravity | Characteristics |
|---|---|---|
| α-white | 1·83 | Cubic crystals. $P_4$ tetrahedral structure |
| β-white | 1·88 | Hexagonal crystals. $P_4$ tetrahedral structure. Formed below −77°C. |
| Amorphous red | 2·16 | Structure unknown |
| Crystalline red | 2·31 | Violet. Triclinic |
| Amorphous black | 2·25 | Structure probably a puckered network |
| Crystalline black | 2·69 | Orthorhombic with a layer-type structure |

From the information at present available it may be concluded that the modifications of phosphorus which have been definitely established are those shown in Table VII.

## The Relative Stability of Phosphorus Allotropes

White phosphorus is the most reactive and crystalline black phosphorus is the least reactive of the forms of elemental phosphorus. There is, however, considerable difference of opinion as to which is the most stable modification. Bridgman[133] found that between 350° and 450°C. black phosphorus had a vapour pressure lower than that of the red form and concluded that black phosphorus was the more stable variety. Smits and co-workers,[169, 170] however, observed that at temperatures below 560°C. black phosphorus had the lower vapour pressure, whereas at above this temperature the red modification gave the lower values. They concluded that black phosphorus was apparently metastable below 560°C. This was supported by the observation that the triple point of black phosphorus was slightly below that of the red variety and that the vapour pressure of black phosphorus in the lower temperature range was not constant, but increased slowly with time. However, the vapour pressure data of these two investigators do not overlap and on plotting the values of $\log p$ against $1/T$ two lines of different slope are obtained, from which differing heats of vaporization can be calculated. The Bridgman data agree better with the supposition that black phosphorus is the more stable form than do those of Smits.

In a more recent investigation[164] the heat evolved per gram-atom when the various forms of phosphorus react with bromine in carbon disulphide has been measured. The results are given in Table VIII (see also page 192).

*Table VIII.—Heats of Reaction of Phosphorus Allotropes with Bromine at 20°C.*[164]

| Form of phosphorus | Heat of reaction (kcal./g.-atom) |
|---|---|
| Crystalline black | 36·6 |
| Amorphous black | 44·1 |
| Bridgman's black | 38·3 |
| Commercial red | 42·2 |
| Laboratory red | 42·5 |
| White | 59·5 |

The laboratory red phosphorus was made by heating white phosphorus at 300°C. and 6000 atm. pressure.

The above results suggest that white phosphorus is the least stable, red next and crystalline black phosphorus is the most stable. The difference between the heats of reaction of crystalline black phosphorus and Bridgman's material was attributed to the presence of some amorphous material in the latter sample.

The densities and chemical stability (except possibly for amorphous black phosphorus) also seem to imply that crystalline black phosphorus is the most stable. This is followed by red phosphorus (triclinic, form V), amorphous black phosphorus and the white form.

Most thermodynamic properties are referred to white phosphorus as their basis. In some reports, however, triclinic red phosphorus has been preferred.[171–2]

## GENERAL PHYSICAL PROPERTIES

In the following data, 'amorphous phosphorus' refers to the ordinary commercial or laboratory made material and not to the amorphous phosphorus form I, referred to above, unless specifically stated.

### Density

The densities of solid phosphorus are given in Table IX.

*Table IX.—The Density of Solid Forms of Phosphorus*

| Variety | Density (g./c.c.) | Ref. |
|---|---|---|
| α-white | $d_4^{20} = 1{\cdot}8233$ $d_4^{44\cdot2} = 1{\cdot}8079$ | 173 |
| β-white | 1·88 | 174 |
| Amorphous—Form I | 2·16 | 131 |
| Amorphous red | 2·20–2·34 | |
| Triclinic—Form V | 2·31 | 131 |
| Amorphous black | 2·25 | 164 |
| Crystalline black | 2·69 | 133, 162 |

The density and atomic volume of white phosphorus at low temperatures have been determined with the results shown in Table X.

*Table X.—Density and Atomic Volume of White Phosphorus*[175]

| Temp. (°C.) | Density (g./c.c.) | Atomic vol. (c.c.) |
|---|---|---|
| −273 | 2·01 | 15·4 |
| −195 | 1·994 | 15·6 |
| −79 | 1·891 | 16·4 |
| +19 | 1·824 | 17·0 |

The values for the density of white phosphorus given above, with the exception of the density at −195°C. which appears to be anomalous, are represented with a maximum error of 0·2% by the equation

$$d_t = 1{\cdot}838 - 6{\cdot}5 \times 10^{-4} t \qquad (t = -273° \text{ to } +44°\text{C.})$$

where $d_t$ is the density at $t$°C. This gives a mean coefficient of cubical expansion of $3{\cdot}53 \times 10^{-4}$.

The atomic volumes of red ($d_{16°} = 2{\cdot}33$) and black phosphorus ($d_{16°} = 2{\cdot}70$) are 13·2 and 11·4, respectively, at −273°C.[175] (see also page 216).

White phosphorus has an expansion of 3·26% on melting.[173] The density of the liquid for the temperature range 20° to 280°C. has been given as[176]

$$d_4^t = 1{\cdot}76705 - 9{\cdot}222 \times 10^{-4}(t-20)$$

Another equation covering the range 7° to 68°C. is[177]

$$d = 1{\cdot}78685 - 9{\cdot}386 \times 10^{-4} t$$

Measurements of the liquid density between 100°C. and 280°C.[178] have been combined with those below 70°C.[177] to give the equation[155]

$$d = 1{\cdot}7862 - 9{\cdot}195 \times 10^{-4} t$$

This equation is valid between 10° and 280°C. and represents the data with an average error of 0·02% and a maximum error of 0·04%.

These equations give a mean coefficient of cubical expansion of liquid phosphorus between 10° and 280°C. of $5{\cdot}18 \times 10^{-4}$. This is substantially in agreement with data previously recorded (Mellor, VIII, 759).

Somewhat lower values for the liquid density have been reported[179] for white phosphorus saturated with water. These data are represented by the equation

$$d = 1{\cdot}782 - 9{\cdot}0 \times 10^{-4} t \qquad (t = 45° \text{ to } 95°\text{C.})$$

Other data for the density of solid and liquid white phosphorus are given in Table XI (see also page 215).

*Table XI.—Density of Solid and Liquid White Phosphorus*

| Temp. (°C.) | Density (g./c.c.) | |
|---|---|---|
| | Solid | Liquid |
| 0 | 1·83676 | — |
| 20 | 1·82321 | — |
| 35 | — | 1·763 |
| 44·4 | — | 1·74529 |
| 100 | — | 1·69490 |

The following equation, which has been derived for the effect of pressure on the specific volumes of liquid and solid states of metals, has been found to apply also to phosphorus.[180]

$$\frac{\mathrm{d}(\Delta v)}{\mathrm{d}p} = \frac{\mathrm{d}T}{\mathrm{d}p}\left[\left(\frac{\partial V_e}{\partial T}\right)_p - \left(\frac{\partial V_s}{\partial T}\right)_p\right] + \left[\left(\frac{\partial V_e}{\partial p}\right)_T - \left(\frac{\partial V_s}{\partial p}\right)_T\right]$$

where $p$ is the pressure, $\Delta v$ the change in volume, $T$ is the transformation temperature and $V_s$ and $V_e$ are the specific volumes of solid and liquid respectively.

The ratio of the density of liquid phosphorus at its triple point to the density at the critical temperature has been given as 2·7.[181]

Red and black phosphorus, on melting, give a liquid which yields white phosphorus on cooling. The vapour pressure curves of red and white phosphorus in the liquid state seem to be different portions of the same curve. It seems likely therefore that there is no distinction to be made between liquid red, liquid black and liquid white phosphorus.[149, 155]

## Melting Point

The melting point of $\alpha$-white phosphorus is generally given as 44·1°C.[155, 174, 182] However, the determination of the melting point is subject to certain errors. Traces of arsenic and sulphur lower the melting temperature. Owing to the high molecular depression of freezing point—41°C. for 1000 g. of solvent—phosphorus of at least 99·996% purity is required if the melting point is to be accurate to within 0·1°C. Supercooling, to which phosphorus is very prone, must also be avoided. Taking these factors into account, the most accurate value for the melting temperature is 44·25° ± 0·05°C. at atmospheric pressure.[173] The pressure dependence of the melting point is 0·0313°C. per atmosphere, and the effect of pressure is given with a maximum error of 0·5% by the equation

$$t = 44{\cdot}22 + 0{\cdot}030p - 0{\cdot}77 \times 10^{-6}\, p^2$$

where $t$ is the melting point in °C. and $p$ is the pressure in kg. cm.$^{-2}$. This equation[183] agrees with data obtained at pressures up to 6000 kg. cm.$^{-2}$

The melting point of red phosphorus has been given various values between 590° and 600°C.[141, 149, 155, 174] However, it appears that the true melting point coincides with the triple point, i.e. 589·5°C. at 43·1 atmospheres.[184–5] Black phosphorus is reported to melt at about 610°C.[133]

## Boiling Point, Critical Temperature and Pressure

The accepted value for the boiling point of white phosphorus is 280·5°C. at atmospheric pressure. The critical temperature and pressure are 695°C. and 82·2 atmospheres respectively.[185]

Rapid transformation of white into red phosphorus occurs between 350° and 500°C. and here liquid phosphorus does not exist.

## Supercooling and Velocity of Crystallization

Liquid white phosphorus has a marked tendency to supercool and can be kept indefinitely in the liquid state at room temperature. Droplets of 1 mm. diameter have been cooled to as low as −71·3°C. before solidification occurred. There is no evidence of glass formation at this temperature.[186]

This supercooling phenomenon has been explained in terms of spontaneous nucleation, the free energy of nucleus formation and the interfacial tension between the solid and the liquid.[187]

The velocity of crystallization at 21·3°C. of the supercooled liquid is 210 cm. sec.$^{-1}$ The temperature dependence of the crystallization velocity $V$ in cm./sec. is given by the equation

$$(\eta V)^{\frac{1}{2}} = 1{\cdot}01\,(44{\cdot}1 - t)$$

where $t$°C. is the temperature and $\eta$ is the viscosity in centipoises.[188]

The theory of crystal growth has been discussed,[189] but the equation derived for the velocity of crystallization does not apply to supercooled liquid phosphorus. The calculated value is about a thousand times smaller than the observed velocity.

### Vapour Pressure

Most of the data on the vapour pressure of phosphorus have already been summarized (Mellor, VIII, 761). This information is discussed below in the light of more recent observations.

Values for the vapour pressure of solid white phosphorus are based largely on the measurements of Centnerszwer.[190] These were obtained by a transpiration method in which hydrogen, carbon dioxide, coal gas and iodobenzene were used as gas streams. Except for hydrogen the measurements were carried out at 20°C. only. Some eight or ten determinations were made with each gas and the average of these is 0·0262 mm. at 20°C. The range, however, was from 0·0192 mm. to 0·0347 mm. The data for hydrogen are given in Table XII.

*Table XII.—Vapour Pressure of Solid White Phosphorus*[190]

| Temp. (°C.) | Vapour pressure (mm.) | |
|---|---|---|
| | Average | Range |
| 20 | 0·0253 | 0·0215–0·0309 |
| 25 | 0·0426 | 0·0397–0·0461 |
| 30 | 0·0729 | 0·0594–0·0860 |
| 35 | 0·0889 | 0·0819–0·1090 |
| 40 | 0·1221 | 0·1174–0·1268 |

These values do not give a linear plot of log $p$ against $1/T$. On the other hand the value at 20°C. seems to be reliable and the free energy of sublimation calculated from the sublimation pressure at 25°C. is in close agreement with that calculated from spectroscopic and calorimetric data combined with independent vapour pressure data (see below).

MacRae and Van Voorhis,[182] who made accurate measurements of the vapour pressure of liquid phosphorus (not of solid phosphorus as is sometimes reported) considered that the most accurate value for the vapour pressure of the liquid at 41·1°C. was 0·181 mm. They combined this with the value (0·0253 mm.) which Centnerszwer obtained at 20°C. and calculated the vapour pressure of solid white phosphorus to be given by the equation

$$\log_{10} p_{\text{mm.}} = 9{\cdot}6511 - 3297{\cdot}1T^{-1}$$

MacRae and Van Voorhis obtained a vapour pressure of 0·173 mm. at 44·1°C. Using this value and an expression for the heat of sublimation the following equation has been derived[155]

$$\log_{10} p_{\text{mm.}} = 1{\cdot}9198 - 3{\cdot}084\times10^{-3}T + 2{\cdot}7763\log T - 2{\cdot}641\times10^{3}T^{-1} - 3{\cdot}258\times10^{4}T^{-2}$$

Another and similar equation based on $p_{\text{mm.}} = 0{\cdot}181$ at the melting point is

$$\log_{10} p_{\text{mm.}} = 1{\cdot}9499 - 3{\cdot}0838\times10^{-3}T + 2{\cdot}8242\log T - 2{\cdot}6829\times10^{3}T^{-1} - 3{\cdot}2521\times10^{4}T^{-2}$$

The additional data used in this calculation are:

(1) heat of vaporization of $P_4 = 12{,}612$ g.-cal. mole$^{-1}$
(2) heat capacity of $P_4$ vapour[191]
(3) heat capacity of solid and liquid phosphorus[192]
(4) heat of fusion of $P_4 = 601$ g.-cal. mole$^{-1}$.[192]

The equation can be simplified, without loss of accuracy, to[173]

$$\log_{10} p_{\text{mm.}} = 8{\cdot}7011 - 2996{\cdot}2T^{-1}$$

Three determinations of the vapour pressure[193] have given the values of 0·0027, 0·0085 and 0·0269 mm. at 0°, 10° and 20°C., respectively. The only one in agreement with other data is 0·0269 mm. at 20°C.

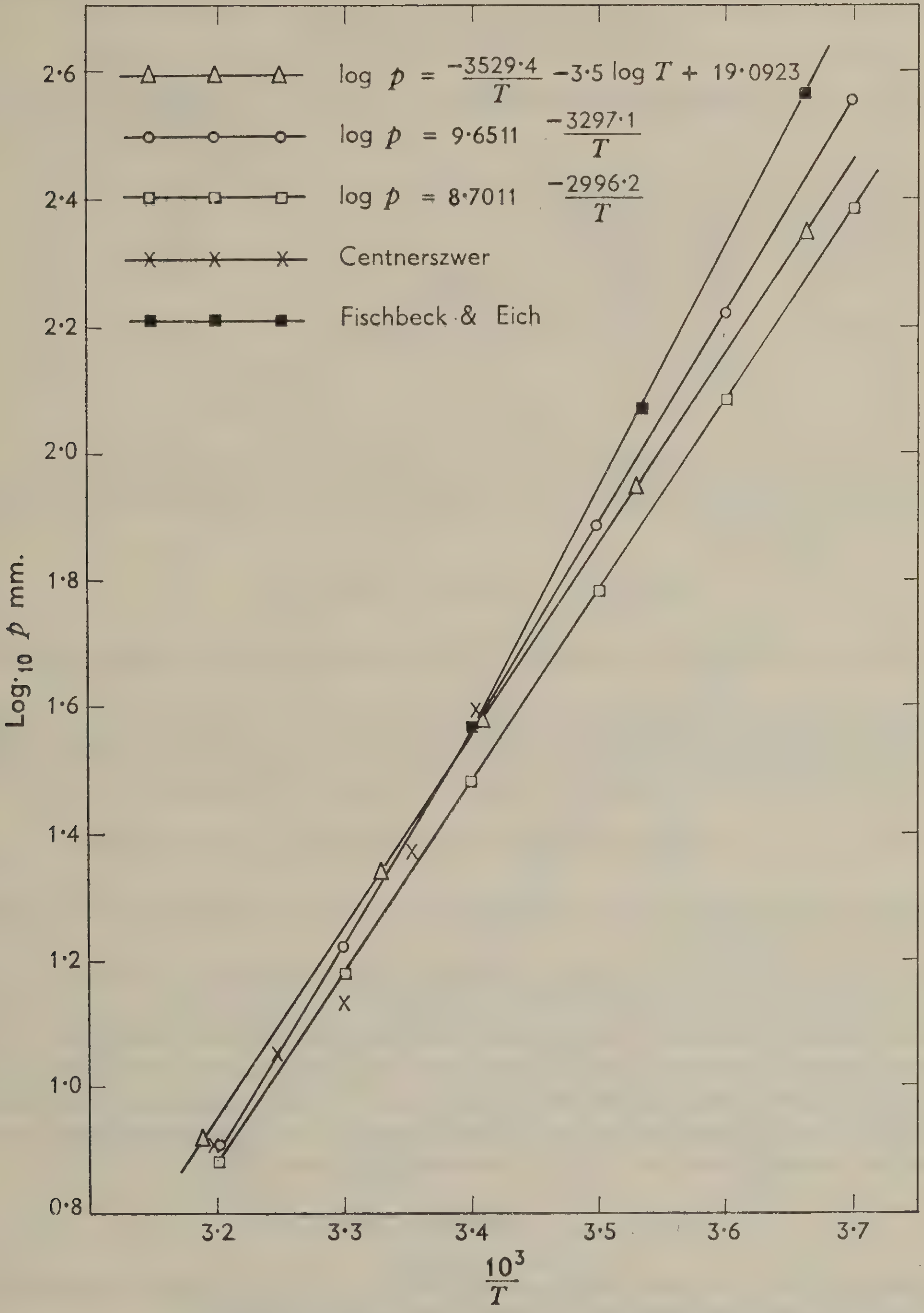


FIG. 5.—Vapour pressure of solid white phosphorus

More recently the vapour pressure has been measured between −23° and 40°C. by a radioactive tracer method.[194] The results were combined with Centnerszwer's value $p_{\text{mm.}} = 0{\cdot}0262$ at 20°C. to give the equation

$$\log_{10} p_{\text{mm.}} = -3529{\cdot}4T^{-1} - 3{\cdot}5 \log T + 19{\cdot}0923$$

The above equations all represent accurately the data to which they refer. However, as shown in Fig. 5 there are significant differences in the slopes of the log $p$

against $1/T$ plots. These differences are shown in Table XIII which gives the heats of sublimation calculated from the equations ($R = 1{\cdot}987$). It would appear that the most reliable value of the heat of sublimation lies between 13·8 and 14·1 kcal. mole$^{-1}$ of $P_4$. It has been calculated from free energy and vapour pressure data that the figure is 14·0 ± 0·3 kcal. mole$^{-1}$ at 25°C.[195]

*Table XIII.—Heats of Sublimation Calculated from the Vapour Pressure Equations of Solid White Phosphorus*

| Vapour pressure equation | Heat of sublimation (kcal. mole$^{-1}$) |
|---|---|
| $\log p_{\text{mm.}} = 19{\cdot}0923 - 3{\cdot}5 \log T - 3529{\cdot}4T^{-1}$ | 14·04 |
| $\log p_{\text{mm.}} = 8{\cdot}7011 - 2996{\cdot}2T^{-1}$ | 13·71 |
| $\log p_{\text{mm.}} = 9{\cdot}6511 - 3297{\cdot}1T^{-1}$ | 15·08 |
| $\log p_{\text{mm.}} = 1{\cdot}9198 - 2641T^{-1} - 32{,}580T^{-2} + 2{\cdot}7763 \log T - 3{\cdot}084 \times 10^{-3}T$ | 13·68 |
| $\log p_{\text{mm.}} = 11{\cdot}920 - 3960T^{-1}$ (data of Fischbeck and Eich) | 18·12 |

The most accurate values for the vapour pressure of liquid phosphorus seem to be those of MacRae and Van Voorhis, which are given for the temperature range 44° to 150°C. by the equation[182]

$$\log_{10} p_{\text{mm.}} = 7{\cdot}9515 - 2757{\cdot}5T^{-1}$$

It should be noted that the constant 7·9515 is sometimes erroneously reported as 7·9542.

The vapour pressure of the liquid has also been measured up to 356°C., at which temperature it is 3·90 atm.[169] Combination of these values with those of MacRae and Van Voorhis and data from other sources[185, 196] gives the equation[155]

$$\log_{10} p_{\text{mm.}} = 18{\cdot}8192 + 1{\cdot}074 \times 10^{-3}T - 3{\cdot}906 \log_{10} T - 3216{\cdot}7T^{-1}$$

which represents the data with an average error of 1·8% and a maximum error of 5·1% between 44° and 360°C.

Liquid yellow phosphorus is rapidly changed to red phosphorus between 350° and 500°C. At temperatures above 500° C. the rate of the reverse change is slow enough to enable the vapour pressure of supercooled red phosphorus to be determined. From the vapour pressure diagram (see Fig. 6 below), it is fairly certain that this phase is identical with liquid white phosphorus. The data[145] from these high temperature measurements are represented by the following equation with a maximum error of 1·1% and an average error of 0·5%,[155] between 504° and 634°C.

$$\log_{10} p_{\text{mm.}} = 7{\cdot}0663 - 2196{\cdot}0T^{-1}$$

This equation gives a vapour pressure of 82·6 atm. for the critical temperature of 695°C. and a pressure of 43·6 atm. at the triple point, 589·5°C.

MacRae and Van Voorhis[182] (Mellor, VIII, 762) found that the vapour pressure measurements for liquid phosphorus between 44° and 634°C. reported by all investigators, with the exception of the data of Schroetter (1844), were given to within ±5% by the equation

$$\log_{10} p_{\text{mm.}} = 11{\cdot}5694 - 2898{\cdot}1T^{-1} - 1{\cdot}2566 \log_{10} T$$

Vapour pressure equations for solid red phosphorus in its various forms have been given above (page 159) for temperatures between 310° and 560°C. The data[184] previously reported (Mellor, VIII, 761) for solid red phosphorus made by heating the white modification for 5 hr. at 550°C., are summarized by the equation[155, 169]

$$\log_{10} p_{\text{mm.}} = 11{\cdot}0844 - 5667{\cdot}7T^{-1}$$

This equation agrees with the data to within ±5% between 280° and 590°C.

The available data[133, 170, 183] on the vapour pressure of solid black phosphorus are summarized by the equation

$$\log_{10} p_{\text{mm.}} = 13{\cdot}14 - 7400T^{-1}$$

which applies in the temperature range of 350° to 590°C. with an average error of 8·5% and a maximum error of 17%.

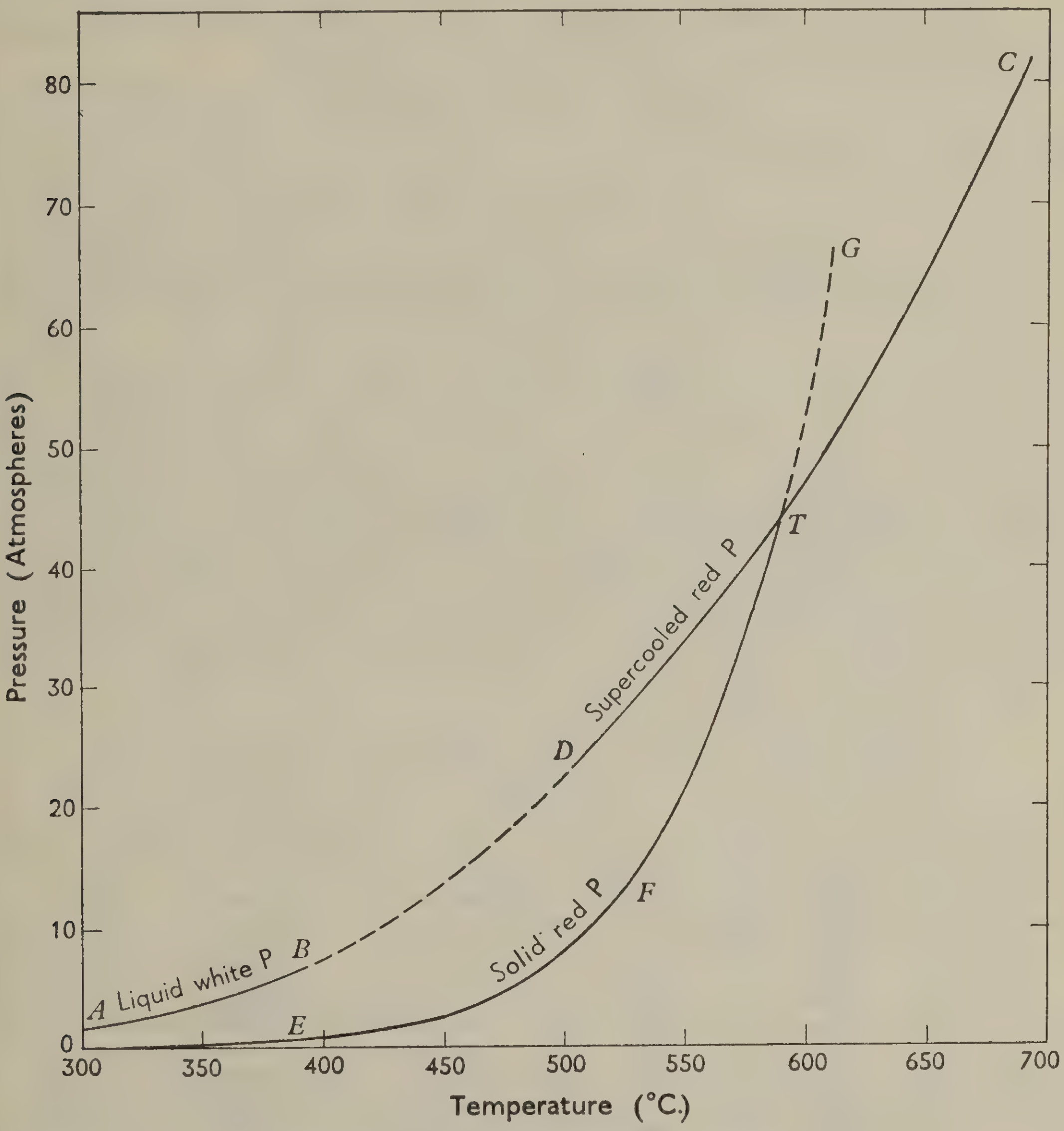


FIG. 6.—Vapour pressure of phosphorus

The vapour pressure data are shown in Fig. 6 for temperatures between 300°C. and the critical point (see also Mellor, VIII, 751–2, and ref. 173, p. 497). Curve *AB* represents the vapour pressure of molten white phosphorus up to nearly 400°C. This is followed by the portion *BD* for which no measurements are available. *TC* is the vapour pressure of molten red phosphorus, measured up to 634°C. and 58·6 atm. and produced to the critical temperature *C* at 695°C. *TD* gives the data for supercooled red phosphorus from the triple point *T* down to the lowest temperature (504°C.) at which measurements could be made. This portion, which is continuous with *AB*, indicates that molten white phosphorus is identical with supercooled red. *EFT* is the vapour pressure curve for solid red phosphorus and *TG* represents the effect of pressure on the melting point of the latter. At *T* red phosphorus melts to give a yellow liquid.

### Vapour Equilibria

In the equilibrium $P_4 \rightleftharpoons 2P_2$ between tetratomic and diatomic phosphorus vapour, anomalies in the early vapour pressure measurements were found to be explained if it were assumed that $P_2$ molecules were in equilibrium with red phosphorus.[197] According to this hypothesis, red phosphorus evaporated in $P_2$ units, but the evidence for this was not conclusive (see ref. 173, p. 487). The vapour pressure of red phosphorus has been measured by evaporating it into a vacuum. Application of the Hertz–Knudsen effusion equation $v = pN/\sqrt{2\pi MRT}$, where $v$ is the effusion velocity, $N$ is Avogadro's number, $p$ is pressure in dynes cm.$^{-2}$ and $M$ is the molecular weight,[198] gave values which are represented by the equation

$$\log_{10} p_{\mathrm{mm.}} = 1{\cdot}10 - 4110T^{-1}$$

between 300° and 480°C.

These data are about $10^{-7}$ times those given by static methods. This was explained as being due to the evaporation of $P_2$ molecules which, under the conditions of the experimental measurements, had no opportunity to recombine as $P_4$ molecules.[199]

The earlier data on the dissociation of phosphorus vapour obtained by Preuner and Brockmöller[200] and by Stock, Gibson and Stamm[201] have already been summarized (Mellor, VIII, 757). At that time there were no means of deciding which were the more reliable data, although it is to be noted that Preuner and Brockmöller considered that their measurements were only approximate. They concluded that there were measurable amounts of $P_4$, $P_2$ and P molecules present at temperatures between 800° and 1200°C., whereas Stock and co-workers found that the only dissociation at these temperatures was that of tetratomic into diatomic molecules.

Calculations[77] based on spectroscopic[71–2, 74, 76] and molecular structure[63] data show that the conclusions and measurements of Stock, Gibson and Stamm are correct and substantially free from error. The data of Stock *et al.* are given in Table XIV, together with the calculated equilibrium constant based on the dissociation energy $\Delta H_0^\circ = 53{,}600$ g.-cal. per mole.[77]

*Table XIV.—The Dissociation of Phosphorus Vapour*[201]

$P_4 \rightleftharpoons 2P_2$

| Temp. (°C.) | Pressure (mm.) | Vapour density | Degree of dissociation | Constant ($K_{\mathrm{atm.}}$) | $K_{\mathrm{atm.}}$ calc.[77] |
|---|---|---|---|---|---|
| 900 | 606 | 58·7 | 0·05 | 0·00717 | 0·00645 |
| | 433 | 58·9 | 0·05 | 0·00440 | |
| | 243 | 57·8 | 0·07 | 0·00520 | |
| | 99 | 55·0 | 0·12 | 0·00600 | |
| 1000 | 691 | 55·5 | 0·11 | 0·0430 | 0·0375 |
| | 498 | 55·2 | 0·11 | 0·0330 | |
| | 283 | 53·4 | 0·15 | 0·0351 | |
| | 119 | 50·0 | 0·23 | 0·0349 | |
| 1100 | 804 | 51·1 | 0·20 | 0·1890 | 0·167 |
| | 586 | 50·3 | 0·22 | 0·1582 | |
| | 339 | 47·7 | 0·29 | 0·1603 | |
| | 145 | 43·6 | 0·41 | 0·1515 | |
| 1200 | 950 | 46·0 | 0·34 | 0·600 | 0·612 |
| | 699 | 44·8 | 0·38 | 0·638 | |
| | 412 | 41·7 | 0·48 | 0·629 | |
| | 175 | 38·3 | 0·61 | 0·527 | |

The vapour density in the above table is referred to hydrogen. The degree of dissociation $\alpha$ is calculated from $\alpha=(\delta-\Delta)/\Delta$, where $\delta$ is the normal vapour density (61·47) of phosphorus and $\Delta$ is the measured value, both referred to hydrogen. From these data the dissociation constant was obtained by using the expression

$$K=\frac{4(\delta-\Delta)^2P}{\delta(2\Delta-\delta)}$$

where $P$ is the pressure in atmospheres (ref. 154, p. 15).

The values of $K_{\text{atm.}}$ from Preuner and Brockmöller's measurements at 900°, 1000°, 1100° and 1200°C. are 0·033, 0·105, 0·276 and 0·658, respectively. The calculated values of $K$ in Table XIV are represented by the equation

$$\log_{10} K_{\text{atm.}} = -11{,}505T^{-1}+7{\cdot}582$$

The dissociation into phosphorus atoms, which Preuner and Brockmöller's data indicated, has also been investigated. Values of the equilibrium constant $K$ derived from these data were used to calculate the heat of dissociation $\Delta H_0^\circ$ from the equation

$$\Delta H_0^\circ = -RT\log_e K - RT.\Delta(\log_e N_0-\log_e Q)$$

where $N_0$ is Avogadro's number and $Q$ is the partition function given by

$$Q=\sum_{n=1}^{\infty}\exp.\{-\epsilon_n/RT\}$$

The results are given in column 3 of Table XV.

The equilibrium constant was also calculated from spectroscopic data alone. These show [72–4] that the dissociated state is $^4S$ with a dissociation energy of $D_0^\circ=5{\cdot}008$ e.v. which corresponds to $\Delta H_0^\circ=115{,}450$ g.-cal. mole$^{-1}$ (1 e.v. = 23·053 kcal. mole$^{-1}$). With this value for $\Delta H_0^\circ$, log $K$ and $K$ were found to be as shown in columns 4 and 5 of Table XV.

*Table XV.—The Dissociation,* $P_2 \rightleftharpoons 2P$, *of Phosphorus Vapour*[77]

| Temp. (°C.) | Experimental data | | Spectroscopic data | |
|---|---|---|---|---|
| | $-\log_{10} K_{\text{atm.}}$ | $\Delta H_0^\circ$ g.-cal. | $-\log_{10} K_{\text{atm.}}$ | $K_{\text{atm.}}$ |
| 800 | 4·355 | 49,400 | 20·13 | $7{\cdot}4\times10^{-21}$ |
| 900 | 3·501 | 49,600 | 18·04 | $9{\cdot}1\times10^{-19}$ |
| 1000 | 2·802 | 49,900 | 16·27 | $5{\cdot}4\times10^{-17}$ |
| 1100 | 2·200 | 50,200 | 14·77 | $1{\cdot}7\times10^{-15}$ |
| 1200 | 1·676 | 50,500 | 13·44 | $3{\cdot}6\times10^{-14}$ |

It will be seen that the values of $\Delta H_0^\circ$ derived from the experimental data are not constant and are very much smaller than the spectroscopic dissociation energy. It should be noted that the latter has been reported to be 5·2 e.v.[202] and 5·031 e.v.[75, 203, 204] of which the second value is probably the more reliable.

The above considerations show that dissociation of phosphorus vapour into atoms is negligible at 1200°C., and the spectroscopic values of $K$ in Table XV conform to the equation

$$\log_{10} K_{\text{atm.}} = 4{\cdot}560-26{,}500T^{-1} \qquad (T \text{ in °K.})$$

This gives an average value of $\Delta H^\circ=121{,}200$ g.-cal. mole$^{-1}$ and an equilibrium constant of $K_{\text{atm.}}=5\times10^{-85}$ at 25°C.

Calculations based on the equilibrium have been extended[205] to temperatures up to 3000°C. with the results shown in Table XVI (see also ref. 154, p. 17).

*Table XVI.—The Equilibrium* $P_2 \rightleftharpoons 2P$ *at High Temperatures*[205]

| Temp. °C. | $K_p$ (atm.) | % dissociation $= 100 \times \left(\frac{K}{K+4}\right)^{1/2}$ |
|---|---|---|
| 25 | $2{\cdot}8 \times 10^{-80}$ | $8 \times 10^{-39}$ |
| 727 | $3 \times 10^{-20}$ | $8{\cdot}7 \times 10^{-9}$ |
| 1000 | $9{\cdot}1 \times 10^{-15}$ | $4{\cdot}8 \times 10^{-6}$ |
| 1227 | $1{\cdot}0 \times 10^{-11}$ | $1{\cdot}6 \times 10^{-4}$ |
| 1500 | $4{\cdot}6 \times 10^{-9}$ | $3{\cdot}4 \times 10^{-3}$ |
| 1727 | $3{\cdot}0 \times 10^{-7}$ | $2{\cdot}7 \times 10^{-2}$ |
| 2000 | $7{\cdot}6 \times 10^{-6}$ | $1{\cdot}4 \times 10^{-1}$ |
| 2500 | $8{\cdot}8 \times 10^{-4}$ | 1·48 |
| 3000 | $2{\cdot}5 \times 10^{-2}$ | 7·86 |

The above data are based on $\Delta H_0^\circ = 115{,}450$ g.-cal. mole$^{-1}$ and give the equation

$$\log_{10} K_{\text{atm.}} = 6{\cdot}100 - 25{,}550T^{-1} \qquad (T \text{ in } ^\circ\text{K.})$$

which gives an average of $\Delta H^\circ = 116{,}850$ g.-cal. mole$^{-1}$.

## Rate of Evaporation

The rate of evaporation of white phosphorus into a vacuum between −20°C. and +20°C. has been measured by a radioactive method using $^{32}$P. The results are given in Table XVII, where $i$ is the number of molecules evaporating per second per sq. cm.

*Table XVII.—Rate of Evaporation of White Phosphorus*[206]

| Temp. (°C.) | Evaporation rate ($i \times 10^{-17}$ cm.$^2$ sec.$^{-1}$) | Evaporation coefficient |
|---|---|---|
| −20·3 | 0·78 | 0·74 |
| −13·1 | 1·56 | 0·70 |
| −6·8 | 3·10 | 0·70 |
| −0·3 | 5·90 | 0·71 |
| 0 | 5·14 | 0·59 |
| 1·0 | 3·90 | 0·43 |
| 2·3 | 6·00 | 0·56 |
| 2·7 | 5·90 | 0·53 |
| 3·0 | 6·20 | 0·56 |
| 4·4 | 5·40 | 0·42 |
| 8·0 | 7·00 | 0·40 |
| 12·0 | 12·10 | 0·48 |
| 17·1 | 20·0 | 0·53 |
| 20·2 | 33·0 | 0·67 |
| 20·3 | 27·0 | 0·54 |

of surface and $\alpha$ is the evaporation coefficient,[206] i.e. the fraction of impinging molecules which condense on the surface.[198]

For red phosphorus the following results have been reported, in g. cm.$^{-2}$ sec.$^{-1}$, for an evaporation coefficient of unity.[199]

*Table XVIII.—Rate of Evaporation of Red Phosphorus*[199]

| Temp. (°C.) | Evaporation rate ($m \times 10^6$ g. cm.$^{-2}$ sec.$^{-1}$) |
|---|---|
| 305 | 1·15 |
| 350 | 3·57 |
| 400 | 7·92 |
| 410 | 6·84 |
| 480 | 5·50 |

No evaporation of red phosphorus was observed at 100°C. under 0·5 mm. pressure.[207]

### Compressibility

The compressibilities of white and red phosphorus between pressures of 100 and 500 atm. at 20°C. have been reported previously (Mellor, VIII, 759). The data for red phosphorus refer to material of density 2·15.[208]

At 30°C. the compressibility, i.e. change in volume divided by the applied pressure, for red phosphorus of density 2·348 (at 20°C.) is 5·05 × $10^{-6}$ cm.$^2$ kg.$^{-1}$ under a pressure of 2000 kg. cm.$^{-2}$ and 3·91 × $10^{-6}$ cm.$^2$ kg.$^{-1}$ for a pressure of 12,000 kg. cm.$^{-2}$. At 75°C. the corresponding values are 5·00 × $10^{-6}$ cm.$^2$ kg.$^{-1}$ and 3·97 × $10^{-6}$ cm.$^2$ kg.$^{-1}$. In the same units the respective data for black phosphorus at the same temperatures and pressures are, 2·6 × $10^{-6}$, 1·7 × $10^{-6}$ and 2·6 × $10^{-6}$ and 1·74 × $10^{-6}$.

Measurements at much higher pressures at room temperature gave the results shown in Table XIX.[209, 210]

*Table XIX.—Compressibility of Red and Black Phosphorus*[209–10]

| Pressure (kg. cm.$^{-2}$) | Relative volume | | Compressibility (cm.$^2$ kg.$^{-1}$) × $10^6$ | |
|---|---|---|---|---|
| | Red | Black | Red | Black |
| 1 | 1 | 1 | 1 | 1 |
| 25,000 | 0·903 | 0·935 | 3·88 | 2·60 |
| 30,000 | 0·885 | 0·927 | 3·45 | 2·43 |
| 40,000 | 0·853 | 0·912 | 3·68 | 2·20 |
| 50,000 | 0·829 | 0·899 | 3·42 | 2·02 |
| | | 0·849(b) | | 3·02 |
| 60,000 | 0·809 | 0·837(b) | 3·18 | 2·72 |
| 70,000 | 0·793 | 0·825 | 2·96 | 2·50 |
| 80,000 | 0·780 | 0·816 | 2·75 | 2·30 |
| 90,000 | 0·667(a) | 0·807 | 3·70 | 2·14 |
| 100,000 | 0·660 | 0·799 | 3·30 | 2·01 |

(a) Irreversible change of red to black phosphorus occurs at 85,000 kg. cm.$^{-2}$, with a volume change from 0·773 to 0·670.

(b) Reversible change occurs at 50,000 kg. cm.$^{-2}$

The above data give straight lines if the logarithm of pressure is plotted against the reciprocal of the relative volume. These lines show breaks where transitions occur. The data conform to the empirical equation

$$p_{\text{atm.}} = C \exp.\{B/V\}$$

where $V$ is the relative volume and $B$ and $C$ are constants. From this it can be shown that

$$\log_{10} p_{\text{atm.}} = 2{\cdot}303\, Ad_0(d-1)$$

where $d_0$ is the density at atmospheric pressure and $A$ is the slope of the $\log_{10} p$ against $1/V$ plot.[211]

The compressibility has been used to calculate the atomic radius of white phosphorus from the expression[130]

$$r^3 = \frac{3V_0}{4\pi N} = \frac{3}{4\pi N}\left(V - \frac{\beta R}{\alpha}\right)$$

where $r$ = radius in A.
$V_0$ and $V$ = molecular volume at 0°K. and $T$°K.
$\alpha$ = coefficient of cubical expansion = $36 \times 10^{-5}$
$\beta$ = compressibility in cm.$^2$ dyne$^{-1}$ = $20{\cdot}3 \times 10^{-12}$
$\boldsymbol{R}$ = gas constant in dyne-cm.$^2$ and cm.$^3$ = $8{\cdot}3144 \times 10^7$
$N$ = Avogadro's number.

Putting $V = 17{\cdot}0$ at 290°K., then $V_0 = 12{\cdot}3$ cm.$^3$ and the radius becomes $1{\cdot}70 \times 10^{-8}$ cm. This is considerably larger than the covalent radius (1·10 A.) or the metallic

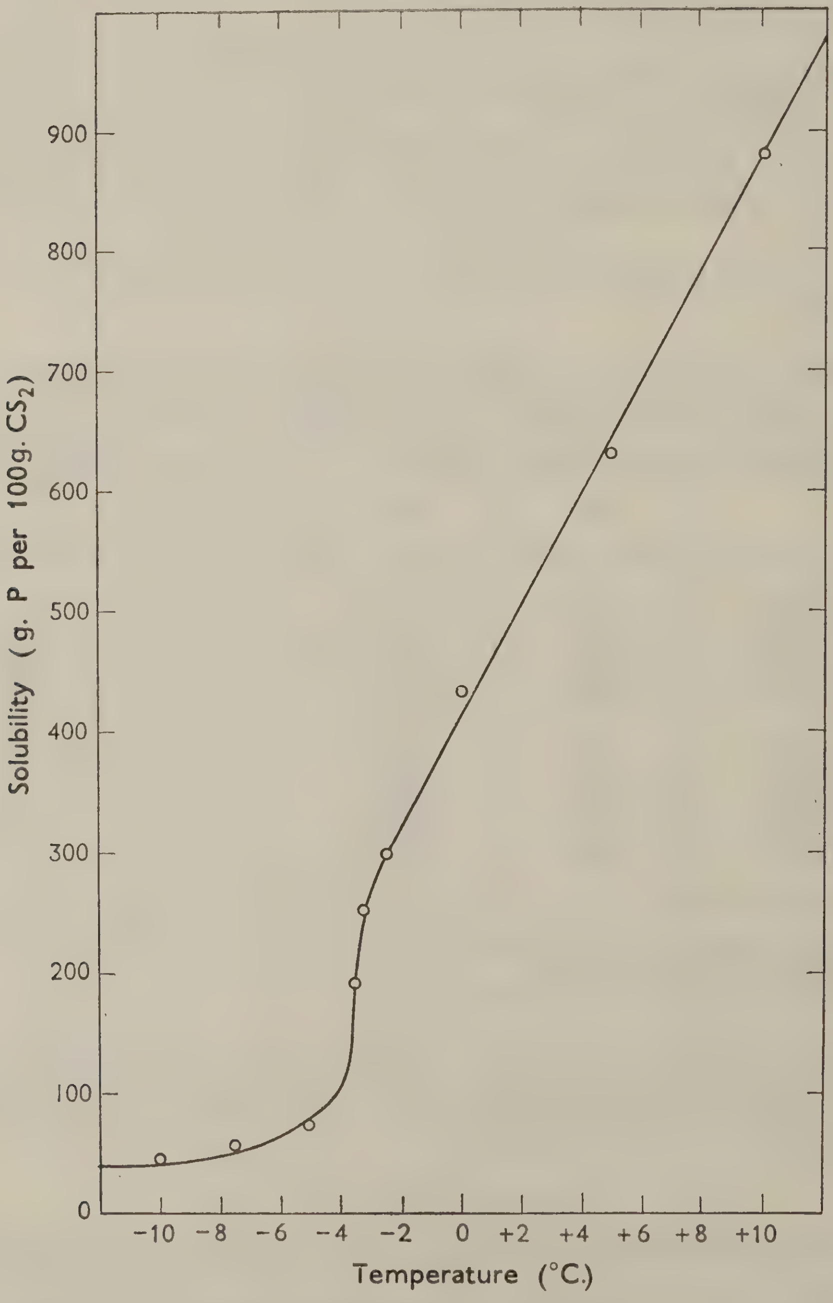


FIG. 7.—Solubility of white phosphorus in carbon disulphide

radius (1·28 A.) of phosphorus.[127] It is more nearly in agreement with the value 1·65 A. given for the radius of a non-bonded phosphorus atom surrounded by twelve neighbours.[128]

### Solubility and Solvent Properties

The solubility of phosphorus in most solvents has already been reported (Mellor, VIII, 789–91). Carbon disulphide is the best solvent and the data previously given for white phosphorus are shown graphically in Fig. 7 where the solubility is expressed as grams of phosphorus per 100 g. of $CS_2$. The break in the curve is attributed to separation of the solution into two immiscible layers between −3°C. and −8°C. It is not due to formation of a compound between phosphorus and the solvent.[212] Below −2°C. the data are not linearly represented by a plot of the logarithm of the solubility against the reciprocal of the absolute temperature.[49] Certain hazards are involved in the dissolution of phosphorus in carbon disulphide, and a suitable technique for doing this has been described.[213]

*Table XX.—Solubility of White Phosphorus in Organic Solvents*

| Temp. (°C.) | Solubility—grams per 100 g. solvent | | | | |
|---|---|---|---|---|---|
| | $CCl_4$ | $n$-$C_7H_{16}$ | $CH_3COCH_3$ | $(C_2H_5)_2O$ | $C_6H_6$ |
| 0 | 0·64 | 0·86 | 0·11 | 0·43 | 1·51 |
| 5 | — | — | — | 0·62 | 1·99 |
| 10 | — | — | — | 0·85 | 2·4 |
| 15 | — | — | — | 0·90 | 2·7 |
| 20 | — | — | — | 1·04 | 3·2 |
| 25 | 1·27 | 1·49 | 0·30 | 1·39 | 3·7 |
| 30 | — | — | — | 1·75 | 4·6 |
| 33 | 1·58 | 1·89 | — | — | — |
| 35 | — | — | — | 2·00 | 5·17 |
| 40 | 1·82 | 2·16 | 0·47 | — | 5·75 |
| 42 | — | 2·23 | — | — | — |
| 45 | 1·96 | — | — | — | 6·11 |
| 46 | — | 2·40 | — | — | — |
| 50 | 2·16 | 2·62 | — | — | 6·8 |
| 51 | 2·19 | — | — | — | — |
| 55 | — | — | — | — | 7·32 |
| 59 | 2·56 | — | — | — | — |
| 60 | — | — | — | — | 7·90 |
| 63 | — | 3·27 | — | — | — |
| 65 | — | — | — | — | 8·4 |
| 70 | — | — | — | — | 8·9 |
| 71 | — | 3·72 | — | — | — |
| 72 | 3·16 | — | — | — | — |
| 75 | — | — | — | — | 9·4 |
| 84 | — | 4·50 | — | — | — |
| 91 | 4·10 | — | — | — | — |
| 94 | 4·23 | — | — | — | — |
| 100 | 4·55 | 5·66 | — | — | — |
| 131 | — | 7·58 | — | — | — |

The solubility of white phosphorus in carbon tetrachloride,[214] $n$-heptane and acetone[215] are given in Table XX. The data for benzene and diethyl ether previously recorded (Mellor, VIII, 790) are included for comparison.

Since liquid white phosphorus has a very high internal pressure, which is much larger than that of most non-polar solvents, solutions of phosphorus show very large deviations from Raoult's law. It has been shown[214] that the solubility in organic solvents can be calculated from the equation

$$RT \log_e \left(\frac{a}{N_2}\right) = V_2\left(\frac{N_1V_1}{N_1V_1+N_2V_2}\right)^2(\delta_2-\delta_1)^2$$

where $a$ = activity of phosphorus referred to the pure liquid
$N_1$ = molecular fraction of solvent
$N_2$ = molecular fraction of phosphorus
$V_1$ = molar volume of solvent at $T$°K.
$V_2$ = molar volume of phosphorus at $T$°K.

$\delta_1$ and $\delta_2$ are the solubility parameters at $T$°K. of the solvent and phosphorus respectively and are a measure of the internal pressures. The parameters are given by the relation

$$\delta = \sqrt{\frac{\Delta E}{V}}$$

where $\Delta E\,(=\Delta H - RT)$ is the molar energy of vaporization. The activity is obtained from the expression

$$\log_e a = \frac{-\Delta H^F}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

in which $T_m$ is the m.p. (317·4°K.) of phosphorus and $\Delta H^F$ the molar heat of fusion. This molar heat was computed from the equations for heat capacity of solid and liquid phosphorus and the heat of fusion (601 g.-cal. mole$^{-1}$) at the melting point, which lead to the equation

$$\Delta H^F = 10{\cdot}523T - 8{\cdot}40\times10^{-3}T^2 - 1{\cdot}31\times10^{-5}T^3 - 1473 \text{ g.-cal. mole}^{-1}$$

The values of the activity at 0° and 25°C. are 0·863 and 0·947, respectively.

The solubility equation cannot be solved directly, but a graphical solution may be obtained by inserting arbitrary values of $N_2$ in both sides of the equation and determining the point of intersection of the resulting curves.[214] A practical measure for interpolating or extrapolating solubilities is to calculate $\delta_2 - \delta_1$, for two or more temperatures. These values are then plotted against the temperature and a straight line drawn through the points.[216] Molecular volume and solubility parameter data are given in Table XXI.[215]

*Table XXI.—Molecular Volumes and Solubility Parameters of Phosphorus*[215]

| Solvent | Molecular volume (c.c.) | | | | Solubility parameter $\delta_1$ | | | |
|---|---|---|---|---|---|---|---|---|
| | 0°C. | 25°C. | 40°C. | 75°C. | 0°C. | 25°C. | 40°C. | 75°C. |
| $CS_2$ | 58·8 | 60·6 | 61·8 | — | 10·27 | 9·92 | 9·70 | — |
| $C_6H_6$ | — | 89·3 | 91·1 | 95·1 | — | 9·16 | 8·94 | 8·4 |
| $CCl_4$ | 94·2 | 97·2 | 99·0 | 103·5 | 8·90 | 8·58 | 8·38 | 7·92 |
| $n$-$C_7H_{16}$ | 143 | 147·5 | 150·2 | 157·6 | 7·76 | 7·43 | 7·24 | 6·78 |
| $(C_2H_5)_2O$ | 100·6 | 104·5 | 107·2 | — | 7·92 | 7·56 | — | — |

More recent data on the solvent powers of paraffin hydrocarbons suggest that a more accurate value of the solubility parameter of $n$-heptane is 8·1 at 25°C.[217] The molar energies of vaporization used to obtain values of $\delta_1$ were calculated from the following equations

$CS_2$ $\quad \Delta E = 8810 - 9{\cdot}6T$
$CCl_4$ $\quad \Delta E = 10990 - 12{\cdot}9T$
$C_6H_6$ $\quad \Delta E = 12100 - 15{\cdot}4T$
$n$-$C_7H_{16}$ $\quad \Delta E = 13490 - 17{\cdot}9T$
$(C_2H_5)_2O$ $\quad \Delta E = 10960 - 17{\cdot}0T$

The molecular volumes of $P_4$ at 0°, 25°, 40° and 75°C. are 69·4, 70·4, 70·9 and 72·3, respectively. The solubility parameters $\delta_2$ for phosphorus, as determined from the solubility in various solvents, are given in Table XXII. No value is given for carbon disulphide at 25°C. because the solubility at this temperature is ideal.[215]

For practical purposes an average value of $\delta_2 = 14{\cdot}4$ may be used for all solvents.[218, 219] It should be noted that values of $\delta_2$ calculated from the molar energies of vaporization (for $P_4, \Delta E = 15{,}135 - 8{\cdot}87T$) are smaller than those derived from the actual solubility data.[215]

*Table XXII.—Solubility Parameters of Phosphorus in Various Solvents*[215]

| Solvent | Solubility parameter $\delta_2$ | |
|---|---|---|
| | at 0°C. | at 25°C. |
| $CS_2$ | 15·0 | — |
| $C_6H_6$ | — | 14·9 |
| $CCl_4$ | 15·0 | 14·5 |
| $n$-$C_7H_{16}$ | 13·9 | 13·5 |
| $(C_2H_5)_2O$ | 14·6 | 13·9 |

If the solubility is plotted in terms of log $X$ against log $T$, where $X$ is the mole fraction of $P_4$ dissolved and $T$ is the absolute temperature, straight lines are obtained, as shown in Fig. 8. The slope of the line gives the entropy of solution.[220]

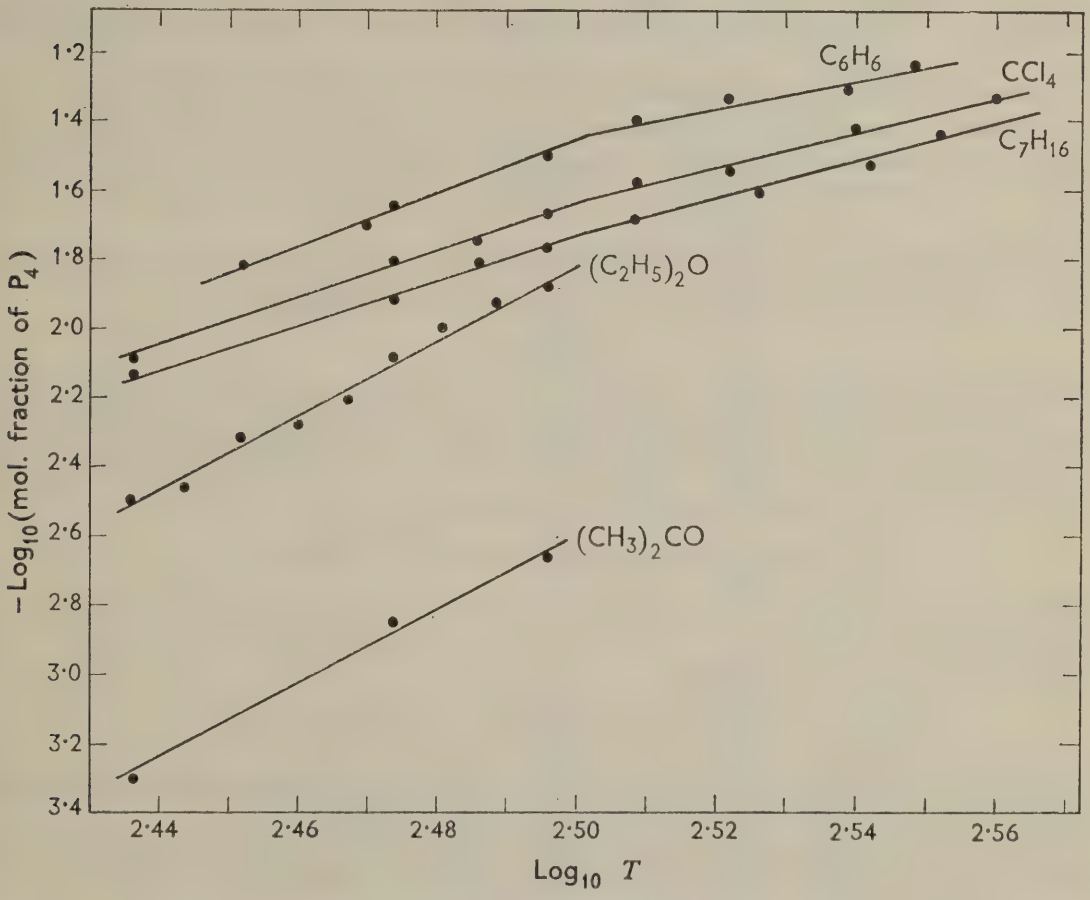


FIG. 8.—Solubility of phosphorus in organic solvents

For those solvents in which the solubility can be measured above the melting point of phosphorus, a break in the curve is found, giving two straight lines which intersect at the melting temperature.[221]

Solubility data for solvents in which phosphorus is only slightly soluble are given in Table XXIII. For information on other solvents and the critical solution temperatures of phosphorus in various liquids, reference should be made to Mellor, VIII, 780–91.

*Table XXIII.—The Solubility of Phosphorus in Miscellaneous Solvents*

| Solvent | Temp. (°C.) | Solubility (g./100 g. solvent) | Ref. |
|---|---|---|---|
| Water | 15 | 0·00033 | 222 |
| Ethyl iodide | 20 | 6·2 | 150 |
| Butyl iodide | 20 | 4·1 | 150 |
| Amyl iodide | 20 | 3·4 | 150 |
| Phenyl iodide | 20 | 5·0 | 150 |
| Phenyl bromide | 20 | 1·9 | 150 |
| Phenyl chloride | 20 | 1·9 | 150 |
| α-Iron | 400 | 0·7 | 223 |
| α-Iron | 700 | 1·2 | 223 |
| α-Iron | 1000 | 4 | 223 |

White phosphorus is readily soluble in molten antimony tribromide, but is quickly converted to red phosphorus which is much less soluble.[224]

Phosphorus is a solvent for thallium, the latter dissolving to the extent of 25 atomic-% to form a solid solution.[225] At 25°C., 0·0285 g. of mercury dissolves in 100 g. of phosphorus under water. The solubility is 0·0338 g. in 100 g. of dry phosphorus.[226] Water is said to dissolve in phosphorus to the extent of about 0·36 g. per 100 g. of phosphorus.[227] Since phosphorus has a cryoscopic constant of 41·3 the presence of 0·36% of water should lower the melting point by 8·25°C., but this has not been observed. The difference between the densities of liquid phosphorus and liquid phosphorus saturated with water (see page 162) corresponds to a solubility of about 0·24 g. of water per 100 g. of phosphorus at temperatures between 40° and 60°C.

Liquid phosphorus at 45°C. has been used as a component in systems having seven,[228] eight,[229] nine,[230] and ten[221] liquid phases in equilibrium.

## Viscosity

The viscosity of liquid white phosphorus has been measured[231] in the temperature range 18° to 80°C., and also between 20° and 140°C.[232] The results of the two sets of measurements are in agreement and give a continuous curve if log $\eta$ is plotted against $1/T$. This curve can be represented by the equation[155]

$$\log_{10} \eta \text{ (centipoise)} = 514{\cdot}4T^{-1} - 1{\cdot}3879$$

which has an average error of 1·08% and a maximum error of 3·1% from the observed values.

The equation (ref. 173, p. 486)

$$\log_{10} \eta \text{ (centipoise)} = 9 \times 10^4 T^{-2} - 10{\cdot}67T^{-1} - 0{\cdot}6318$$

agrees more closely with the data up to 90°C. but over the whole temperature range has an average error of 1·4% and a maximum error of 4·0%.

The data show some scatter, particularly between 40° and 80°C., and the best straight line through the points appears to be given by the equation

$$\log_{10} \eta \text{ (centipoise)} = 526{\cdot}3T^{-1} - 1{\cdot}4273$$

which has a maximum error of 3·5% and an average error of 1·3%.

The viscosity of molten white phosphorus saturated with water is reported[233] to be represented by the equation

$$\eta \text{ (centipoise)} = 3{\cdot}314 - 9{\cdot}65 \times 10^{-2}t + 1{\cdot}279 \times 10^{-3}t^2 - 5{\cdot}76 \times 10^{-6}t^3$$

where $t$ is in the range 45° to 95°C. Data calculated from this equation are 60% (at 45°C.) to 74% (at 95°C.) of the values given above. In view of the low solubility of water in liquid phosphorus the effect on the viscosity seems anomalous.

Calculated values for the viscosity of phosphorus vapour are given on page 212.

### Surface Tension and Parachor

The surface tension of liquid white phosphorus is given in Table XXIV. These values give a parachor of 204·8 c.c. for the $P_4$ molecule[234, 235] (see also page 213).

*Table XXIV.—Surface Tension of Liquid White Phosphorus*

| Temp. (°C.) | Surface tension (dynes cm.$^{-1}$) |
|---|---|
| 50 | 69·70 |
| 54 | 68·53 |
| 60·2 | 66·95 |
| 68·7 | 64·95 |

These measurements were made by a bubble pressure method in an atmosphere of carbon dioxide. The data previously reported (Mellor, VIII, 759) were obtained by a capillary rise method and in calculating the surface tension it was assumed that the angle of contact between phosphorus and glass was zero. This angle is in fact not zero so that the previous values for the surface tension are too small.

*Table XXV.—Interfacial Tension between Phosphorus and Various Liquids*

| Liquid | Temp. (°C.) | Interfacial tension (dynes cm.$^{-1}$) |
|---|---|---|
| Water | 46·0 | 52·9 |
| | 52·8 | 51·2 |
| | 61·0 | 49·7 |
| | 64·0 | 48·1 |
| | 71·0 | 46·7 |
| Benzene | 52 | 13·0 |
| | 60 | 12·5 |
| | 67 | 11·5 |
| *cyclo*Hexane | 50 | 18·1 |
| | 58 | 17·9 |
| | 69 | 17·2 |
| *n*-Hexane | 50 | 23·3 |
| | 60 | 23·7 |
| Ethanol | 50 | 29·7 |
| | 60 | 27·9 |
| | 68 | 27·4 |
| Acetone | 46·5 | 29·4 |
| | 50 | 29·1 |
| | 54 | 29·1 |

The interfacial tension between phosphorus and a number of liquids has been measured, with the results[234] shown in Table XXV.

It is reported that phosphorus, unlike sulphur, does not alter the surface tension of liquid iron–carbon–sulphur alloys to any marked degree.[236] The effect of phosphorus is, however, greater than that of silicon.[237]

## Tensile Strength

The ultimate tensile strength of white phosphorus has been measured[238] at temperatures between −5° and 44°C. For this purpose cylindrical rods of phosphorus 13 cm. long and 1·0 cm. in diameter were subjected to a load, starting at zero and increasing at the rate of 2·2 kg./min. until breaking occurred. The value of the breaking load was reproducible to within 4% at any given temperature. At some temperatures there was considerable elongation of the rods before fracture occurred. The elongation was measured with an accuracy of ±2 mm. The data obtained are given in Table XXVI and the effect of temperature on the tensile strength is shown graphically in Fig. 9.

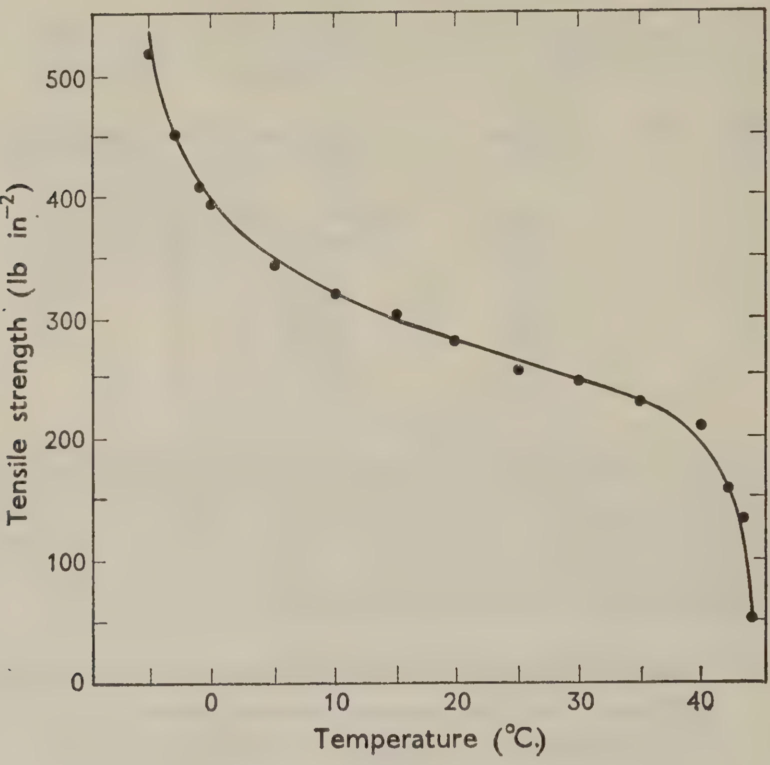


FIG. 9.—Tensile strength of white phosphorus

*Table XXVI.—The Tensile Strength of White Phosphorus*

| Temp. (°C.) | Tensile strength | | Elongation | |
|---|---|---|---|---|
| | (kg. cm.$^{-2}$) | (lb. in.$^{-2}$) | (mm.) | (%) |
| −5 | 36·4 | 517 | 0 | 0 |
| —3 | 31·8 | 451 | 2·3 | 1·8 |
| −1 | 29·0 | 411 | 4·3 | 3·3 |
| 0 | 28·0 | 397 | 6·3 | 4·9 |
| 5 | 24·4 | 346 | 14·3 | 11·0 |
| 10 | 22·6 | 320 | 30·3 | 23·3 |
| 15 | 21·3 | 303 | 41·6 | 32·0 |
| 20 | 19·8 | 280 | 70·3 | 54·1 |
| 25 | 18·1 | 257 | 90·3 | 69·5 |
| 30 | 17·5 | 248 | 95·6 | 73·6 |
| 35 | 16·1 | 229 | 102 | 78·5 |
| 40 | 14·5 | 206 | 88·3 | 67·9 |
| 42 | 11·0 | 156 | 64·6 | 49·7 |
| 43 | 9·3 | 135 | 57·6 | 44·3 |
| 44 | 3·6 | 50 | 35·6 | 27·4 |

Below 0°C. the phosphorus was very brittle and broke suddenly to give a square-ended fracture. Above this temperature there was a gradual decrease in brittleness, this becoming negligible at about 15°C. Between 15° and 35°C. there was a rapid increase in elongation before breakage occurred, and conical fractures were produced. Increased brittleness and decreased elongation were found above 35°C. At all temperatures the phosphorus showed little or no elasticity, and did not recover its original length on removing the load, even when the amount of stretching was only 2 mm.

### Creep

Bending creep in white phosphorus has been reported for temperatures of 27° and 41° at pressures up to 6 kbar.[476] The activation volume for creep is $50{\cdot}3 \times 10^{-24}$ cm.$^3$/atom, which agrees with the value for self-diffusion reported earlier.[240]

### Diffusion

The coefficient of self-diffusion in white phosphorus varies with temperature as shown in Table XXVII.

*Table XXVII.—Self-diffusion in α-White Phosphorus*[239]

| Temp. (°C.) | Diffusion coefficient $D$ (cm.$^2$ sec.$^{-1}$) |
|---|---|
| 0 | $3{\cdot}19 \times 10^{-11}$ |
| 10 | $6{\cdot}07 \times 10^{-11}$ |
| 18·7 | $1{\cdot}07 \times 10^{-10}$ |
| 25 | $1{\cdot}40 \times 10^{-10}$ |
| 30 | $1{\cdot}75 \times 10^{-10}$ |
| 39·4 | $3{\cdot}94 \times 10^{-10}$ |
| 41·3 | $4{\cdot}58 \times 10^{-10}$ |
| 41·88 | $5{\cdot}91 \times 10^{-10}$ |
| 42·82 | $8{\cdot}01 \times 10^{-10}$ |
| 43·86 | $> 8 \times 10^{-10}$ |

A plot of log $D$ against $1/T$ deviates from a straight line above 30°C. as shown in Fig. 10. Below this temperature the diffusion coefficient is given by

$$\log_{10} D = -2{\cdot}971 - 2058T^{-1}$$

which gives an activation energy for self-diffusion of 9400 g.-cal. mole$^{-1}$. This agrees with the value found from

$$\Delta E = 16{\cdot}5L$$

where $L$ is the latent heat of fusion and the constant 16·5 applies for a face-centred or body-centred cubic crystal lattice. Below 30°C. the diffusion mechanism is believed to involve vacant sites in the lattice.

Above this temperature the diffusion coefficient is given by

$$\log_{10} D = 46{\cdot}3 - 17{,}635T^{-1}$$

This corresponds to an activation energy of 80,600 g.-cal. mole$^{-1}$ and a very high entropy. These high values are consistent with the supposition that near the melting point there are present liquid microphase regions. These contain, on average, about 130 phosphorus molecules and 10 vacant lattice sites which are the principal centres of diffusion.[239]

Increasing pressure decreases the rate of self-diffusion as shown in Fig. 11 for temperatures of 30°C. and 41·3°C. The slope of the 30°C. graph gives an activation volume of $49{\cdot}7 \times 10^{-24}$ cm.$^3$/atom. At 41·3°C. the activation volume is about

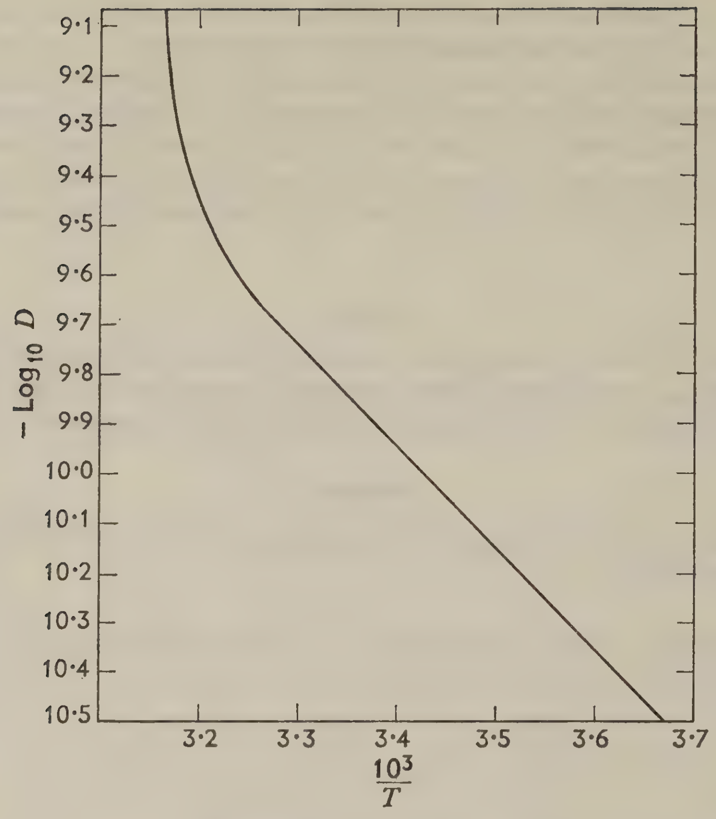


FIG. 10.—Variation of self-diffusion of phosphorus with temperature

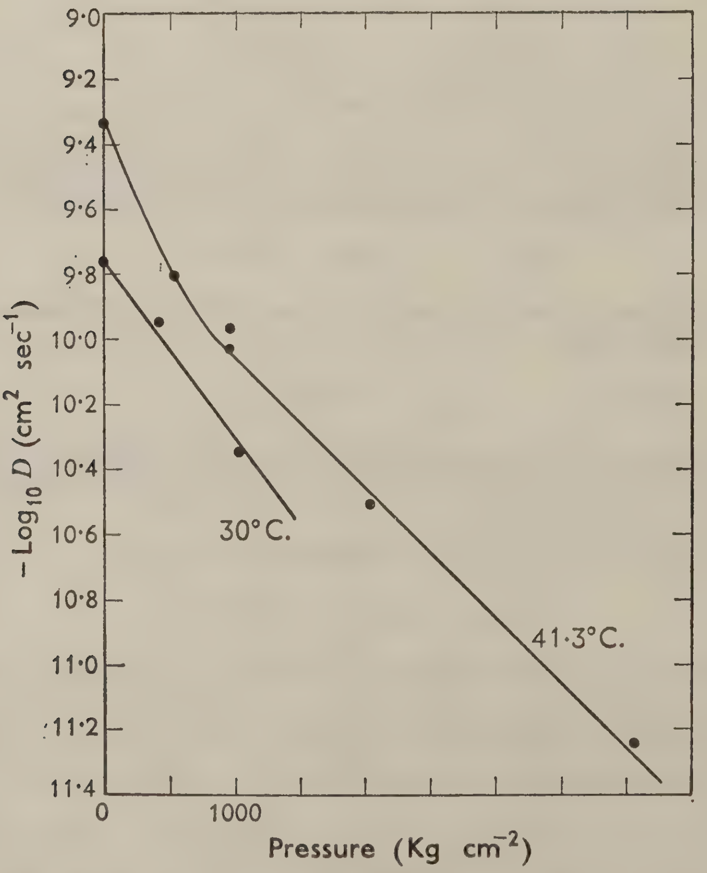


FIG. 11.—Effect of pressure on the self-diffusion of white phosphorus

$348 \times 10^{-24}$ cm.$^3$/atom. These data are interpreted as indicating a large disordering of the crystal lattice which begins well below the melting point of phosphorus.[240] The activation volumes have been used to calculate the entropy of diffusion from the coefficients of thermal expansion and compressibility. Agreement with observed entropy values, however, is not good.[241] The pressure dependence of the diffusion coefficients and the melting point has been reported to be identical for white phosphorus and metallic sodium.[242]

The coefficient of diffusion of phosphorus into copper covered with a layer of cuprous oxide is reported to be $2{\cdot}1 \times 10^{-8}$ cm.$^2$ sec.$^{-1}$ at about 1000°C.[243] At 1020°C. for a cuprous oxide layer about 0·20 mm. in thickness the concentration of phosphorus in atoms/c.c. was found to be $18 \times 10^{16}$, $37 \times 10^{16}$ and $200 \times 10^{16}$ at depths of 0·01, 0·10 and 0·172 mm., respectively.[244]

The diffusion of phosphorus into silicon has been studied in connection with the semiconductor properties of the latter. Conflicting values of the diffusion coefficient have been reported. Diffusion of phosphorus vapour into silicon oxide films 0·1–0·4 $\mu$ in thickness at temperatures of 1125° to 1250°C. is said to occur at a rate agreeing with the equation[245]

$$D = D_0 \exp\{-E/kT\}$$

where $D_0 = 3{\cdot}9 \times 10^{-12}$ cm.$^2$ sec.$^{-1}$, $k$ is Boltzmann's constant and the activation energy is 1·4 electron volts (32 kcal. mole$^{-1}$). This, however, does not agree with the observed value of $D = 2{\cdot}1 \times 10^{-15}$ cm.$^2$ sec.$^{-1}$ at 1150°C. The temperature dependence of $D$, as calculated from the experimental values, is

$$\log_{10} D = -10{\cdot}11 - 6500T^{-1} \quad \text{or} \quad D = 7{\cdot}76 \times 10^{-11} \exp\{-29{,}700/RT\}$$

The above data were interpreted in terms of a two-layer system of silicon and silicon oxide. In another investigation[246] it was shown that at 1100° to 1150°C. a glass of unknown composition $P_xSi_yO_z$ is formed between the silicon and silicon oxide, with a sharp boundary separating the glass from the oxide. An *n–p* junction was formed beneath the glass. The diffusion coefficients $D_1$ and $D_2$ for the diffusion of phosphorus into the glass and into silicon, respectively, are given in Table XXVIII.

*Table XXVIII.—Diffusion of Phosphorus in Silicon*

| Temp. (°C.) | Coefficient $D_1$ (cm.$^2$ sec.$^{-1}$) for PSiO glass | Coefficient $D_2$ (cm.$^2$ sec.$^{-1}$) for silicon |
|---|---|---|
| 1100 | $2 \times 10^{-13}$ | $1{\cdot}8 \times 10^{-12}$ |
| 1150 | $4 \times 10^{-13}$ | $3{\cdot}5 \times 10^{-12}$ |

The coefficient for the diffusion of phosphorus through an oxide layer into silicon is reported to be about $10^{-14}$ cm.$^2$ sec.$^{-1}$ at 1250°C.[247] This is much smaller than the values of $D_2$ for silicon in Table XXVIII, but agrees with the coefficient calculated from

$$\log_{10} D = -10{\cdot}11 - 6520T^{-1}$$

Presumably $10^{-14}$ cm.$^2$ sec.$^{-1}$ represents a coefficient for the diffusion of phosphorus in silicon oxide.

The diffusion of phosphorus from phosphorus pentoxide vapour into silicon at 970° to 1275°C. gives the following equation for the diffusion coefficient[248]

$$\log_{10} D = 1{\cdot}021 - 18{,}600T^{-1}$$

which corresponds to an activation energy of 85,000 g.-cal. mole$^{-1}$. The values of $D$ calculated from this equation are substantially in agreement with those of $D_2$ given above. The diffusion coefficients of phosphorus and boron are almost identical between 950° and 1300°C.,[248, 249] the activation energy of the latter being 81,000 g.-cal. $\text{mole}^{-1}$.[250]

Preliminary values for the diffusion of phosphorus into single crystal silicon, using phosphorus vapour at 1050° to 1250°C. gave diffusion coefficients represented by the equation[249]:

$$\log_{10} D = -3{\cdot}00 - 25{,}200T^{-1}$$

From these measurements, which are not in agreement with the values given above, it was estimated that either $D$ is in error by 50%, or there is a 15% error in the activation energy quoted above. The oxygen content of silicon is reported to have no appreciable effect on the diffusion or solubility of phosphorus in silicon,[251] the measured diffusion rates agreeing with those of ref. 248. Observations on the diffusion of phosphorus vapour in silicon indicate that the solubility of phosphorus in silicon is constant between 900°C. and 1300°C.[252] The diffusion rate at 1200°C.[253] gives a coefficient of $2{\cdot}7 \times 10^{-12}$ $\text{cm.}^2$ $\text{sec.}^{-1}$, in good agreement with the values of Fuller and Ditzenberger.[248] The technique[254, 255] and the thermodynamics[256] of the diffusion of phosphorus in silicon have been discussed.

The diffusion of phosphorus in germanium between 900° and 1200°C. is given by the equation

$$\log_{10} D = 0{\cdot}40 - 12{,}400T^{-1}$$

which gives an activation energy of 56,700 g.-cal. $\text{mole}^{-1}$. Similar activation energies are found for arsenic, antimony, zinc, gallium and indium, but boron has a much higher energy.[257]

The diffusion coefficient for phosphorus in a calcium aluminium silicate melt is reported to be $4{\cdot}4 \times 10^{-6}$ $\text{cm.}^2$ $\text{sec.}^{-1}$ at 1500°C.[258] At 1320°C. for a slag containing CaO 39·4, $Al_2O_3$ 21·2 and $SiO_2$ 38·8% the coefficient is $5{\cdot}7 \times 10^{-5}$ $\text{cm.}^2$ $\text{sec.}^{-1}$ [259]

Phosphorus is reported to migrate in calcium phosphate melts as the $P^{5+}$ ion with a mobility of $3{\cdot}4 \times 10^{-5}$ $\text{cm.}^2$ $\text{volt}^{-1}$ $\text{sec.}^{-1}$ [260]

## OPTICAL PROPERTIES

The refractive index of liquid phosphorus between 44° and 65°C. for sodium light is given by the equation[261]

$$n = 2{\cdot}11038 - 7{\cdot}9 \times 10^{-4}t$$

These values are somewhat smaller than those previously recorded (Mellor, VIII, 763).

The refractive index has also been measured for light of wave-lengths 4358, 5461, 5780 and 6907 A.

The value of $$\frac{(n^2-1)}{(n^2+2)d}$$

where $n$ is the refractive index and $d$ is the density, is constant at 0·3006 for the same range of temperatures. This gives a molar refraction of 37·3 for the $P_4$ molecule (see also page 208 for bond refraction).

White phosphorus becomes doubly refractive on cooling to −75°C., but the reverse change occurs on heating to −68°C. Hexagonal crystals of phosphorus, similar to those of $K_2PtCl_4$, were obtained on crystallizing the element from carbon disulphide at −80°C. or from ether at −100°C.[134]

The activation energy for photoconductivity is 1·40–1·56 electron-volts as compared with a thermal activation energy of 1·51–1·64 e.v. The threshold wave-length for the photoconductivity effect is $\lambda_{1/2}(\mu) = 0{\cdot}85$.[262]

The photoelectroluminescence of zinc sulphide activated by phosphorus has been described.[263] Luminescent flashes are observed when the material is irradiated with infra-red radiation.[264] The luminescence is said to involve a two-step excitation mechanism of long and short wave-lengths.[265]

The photochemical conversion of white phosphorus dissolved in carbon disulphide to red phosphorus is a unimolecular reaction. It is concluded that the dissociation $P_4 \rightleftharpoons 2P_2$ is involved.[266]

## ELECTRICAL AND MAGNETIC PROPERTIES

Most of the electrical and magnetic properties of phosphorus have been reported previously (Mellor, VIII, 766). Ionization potentials are summarized in Table III, page 150 above. The ionization energy of phosphorus as a donor impurity in germanium has been measured[267] by analyzing curves of carrier concentration against $1/T$. The value obtained was 0·0120 e.v.

In silicon the ionization energy of the ground state of phosphorus is 0·0455 e.v. The observed spacing $(2p, m = \pm 1) - (2p, m = 0)$ of the excited electronic levels is 0·0053 e.v., in agreement with the theoretical value of 0·0050 e.v.[268] The theory of the donor levels[269] and the hyperfine splitting of the donor states of phosphorus in silicon has been discussed. The lines observed in the hyperfine structure in *n*-type silicon correspond exactly to the nuclear spin of the added Group V elements. This shows that the electron-spin resonance is due to the resonance of electrons localized near the Group V atoms.[270]

The ionization potential has been used to calculate the atomic radius: a value of 0·44 A. has been obtained for the $P^{3+}$ ion.[271] The paramagnetic resonance of phosphorus in silicon has been studied and two lines separated by about 45 gauss were found.[272] The measured electric field gradient for phosphorus is 9·03, compared with a calculated value of 11·06.[273]

### Electronegativity and Electron Affinity

Electronegativity was first defined by Pauling[123] as the power of an atom or molecule to attract electrons to itself. He found an empirical relation between the energy of a bond and the electronegativities of the bonded atoms. From this he estimated electronegativities, on what is now referred to as the Pauling scale. Other scales of measurement have been proposed[274] but the values of Pauling are generally regarded as being the most useful and reliable for purposes of calculations involving electronegativity. On the Pauling scale the electronegativity of phosphorus is 2·1.

Mulliken[275] defined the atomic electronegativity $M$, for which he used the term electro-affinity, as the average of the ionization potential $I$ and the electron affinity $E$, both in electron volts, i.e.,

$$M = \tfrac{1}{2}[I + E]$$

On this scale the electronegativity of phosphorus is 5·80. Mulliken plotted his values against those of Pauling and found that for most elements his values were 2·78 times those of Pauling, a relationship which fits the data for phosphorus. A more recent evaluation[276] based on revised values of ionization potentials[62] suggests that a better factor is 3·15[274] but this does not correlate the two electronegativity values of phosphorus. Mulliken's values, which take into account the dependence of ionization energies on the orbital characteristics of an atom in a molecule, appear to be better and more precise than the Pauling electronegativity. They are, however, more difficult to apply quantitatively to most elements because of the lack of reliable data on electron affinities. In an extension of Mulliken's ideas, in which ionization potentials and electron affinities are referred to valency states rather than to physically measured values, electronegativity values for three valencies of phosphorus have been calculated[274, 276] with the results shown in Table XXIX.

Electronegativity has also been defined[277] as the potential at a distance $r$ (the covalent radius) from the nucleus which is caused by the nuclear charge effective at that distance. This charge was estimated by assuming that the electrons in the closed shells of an element exerted their full screening power on the nucleus. The screening

*Table XXIX.—Mulliken Electronegativities for Phosphorus*

| Valency state | Ionization potential (e.v.) | Electron affinity (e.v.) | Electronegativity |
|---|---|---|---|
| $s^3p^3, V_3$ | 10·15 | 1·29 | 5·72*p* |
| $sp^4, V_3$ | 11·94 | 2·42 | 7·18*p* |
| $sp^4, V_3$ | 24 | 8·60 | 16·3*s* |

constant of one valence electron for another was taken to be 0·5. The electronegativity, $x$, is then given by the expression

$$x = 0{\cdot}31\left(\frac{n+1}{r}\right)+0{\cdot}50$$

where $n$ is the number of electrons in the valency shell and $r$ is the covalent radius in Ångström units. For phosphorus ($r=1{\cdot}1$) this gives a value of 2·19.

A similar expression

$$x = 0{\cdot}44(z/r)+0{\cdot}28$$

where $z$ is the effective nuclear charge as defined by Slater[278] has also been used.[274] With $r=1{\cdot}1$ and $z/r=4{\cdot}36$ the electronegativity of phosphorus becomes 2·20.

More recently[279] electronegativity has been related to the force of attraction between a nucleus and an electron from a bonded atom. If $r$ is the distance between the nucleus and the electron, and $e$ is the electronic charge, then the charge which is effective at the electron due to the nucleus and its surrounding electrons is $ez$. The force of attraction, which is a measure of the electronegativity, is $F=e^2z/r^2$. A plot of $z/r^2$ against Pauling electronegativities gives the new electronegativity according to the equation

$$x = 0{\cdot}359(z/r^2)+0{\cdot}744$$

Using Slater's values for the effective nuclear charge $z$, then $z/r^2$ is 3·678 for phosphorus and the electronegativity is 2·06.

An alternative method of evaluating electronegativity, based on the stability ratio, has been proposed.[280] The electron density of an element, or the number of electrons per cubic Ångström unit is $3A/4\pi r^3$, where $A$ is the atomic number and $r$ is the covalent radius. The stability ratio, which has a maximum value of 1, is the ratio of the electron density of an atom to that of an iso-electronic inert atom.[281] The stability ratio $S$ is related to the Pauling electronegativity $P$ by the equation[282]

$$P^{1/2} = 0{\cdot}21S+0{\cdot}77$$

For a covalent radius of 1·06 the electron density of phosphorus is 3·04, giving a stability ratio of 3·34. This corresponds to an electronegativity of 2·16 on Pauling's scale.[280]

The electronegativity of cations as measured by the stability ratio has been empirically related to the ionization potential by the equation[283]

$$S = 1{\cdot}54I^{1/2}+c$$

where $S$ is the stability ratio and $c$ is a constant. The value used for $I$ is the sum of the ionization potentials required to form the ion from the neutral atom. For the $P^{5+}$ ion, $c$ is $-1{\cdot}33$ and $I$ is 177·2 (see Table III, page 150), giving 19·1 for $S$. In a similar manner, stability ratios of 3·87, 3·32 and 2·5 have been obtained for the $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$ ions, respectively.

The stability ratios of $PCl_3$, $P_4O_6$ and $P_4O_{10}$ have been reported to be 4·48, 4·36 and 4·59, respectively. The use of these ratios in interpreting chemical variations in the phosphorus halides[284] and in estimating partial charges in an atom of a molecule[285] have been discussed.

The electron affinity, defined as the energy liberated when a negative ion is formed by an atom acquiring an electron, has not been measured directly for phosphorus owing to experimental difficulties. Estimates of 1·33,[286] 1·10,[287] 0·8,[276, 288] 0·77,[289] 0·72,[290] 0·70[291] and 0·57[292] electron volts have been reported for the $P^-$ ion. The best value seems to be 0·72 e.v.

## Dielectric Constant of White Phosphorus

Measurements of the dielectric constant of liquid phosphorus between 34° and 85°C. show that the value of the constant at 45°C. is about 5% greater than that previously reported (Mellor, VIII, 767).

Some representative data for the dielectric constant $\epsilon$ are given in Table XXX.[293] From the Mosotti–Clausius relation

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

the dielectric molar polarization $P$ is 35·9. This agrees with the value of the electron polarization as calculated from the refractive index for sodium light (page 182) for the $P_4$ molecule.

*Table XXX.—The Dielectric Constant of White Phosphorus*

| Temp. (°C.) | Dielectric constant |
|---|---|
| 34·0 | 4·096 |
| 38·1 | 4·082 |
| 41·1 | 4·073 |
| 42·2 | 4·069 |
| 44·0 | 4·064 |
| 46·1 | 4·057 |
| 47·0 | 4·055 |
| 48·0 | 4·052 |
| 48·6 | 4·052 |
| 49·0 | 4·047 |
| 51·3 | 4·039 |
| 55·0 | 4·027 |
| 59·4 | 4·008 |
| 70·4 | 3·961 |
| 76·2 | 3·929 |
| 85·0 | 3·860 |

The above data give a molecular polarizability of $14{\cdot}2 \times 10^{-24}$ Å$^3$. The atomic polarizability, calculated[294] from the expression $\alpha = 2{\cdot}3r^3$ ($r$ = single-bond covalent radius), is $3{\cdot}06 \times 10^{-24}$ Å.$^3$

## The Electrical Properties of Black Phosphorus

Data on the electrical resistance of black phosphorus at temperatures up to 100°C. and pressures up to 12,000 kg. cm.$^{-2}$ have been reported previously (Mellor, VIII, p. 766). It should be noted that the specific resistance at 0°C. is 1·0 ohm per cm. cube and not 1000 as given.[295]

Measurements at 30° and 75°C. at higher pressures show that for both temperatures the resistances at 20,000 kg. cm.$^{-2}$ pressure are less than one-hundredth of the corresponding values at atmospheric pressure. The resistance passes through a minimum at 23,000 kg. cm.$^{-2}$ pressure.[296] The temperature coefficient of resistance changes sign at 12,000 kg. cm.$^{-2}$, becoming positive like that of pure metals at higher pressures.[297]

The resistivity of black phosphorus has been measured between −200°C. and +350°C., with the results shown in Fig. 12.[298]
At temperatures above 0°C. the resistivity $\rho$ in ohm-cm. is given by

$$\rho = 0{\cdot}0030 \exp\{W/2kT\}$$

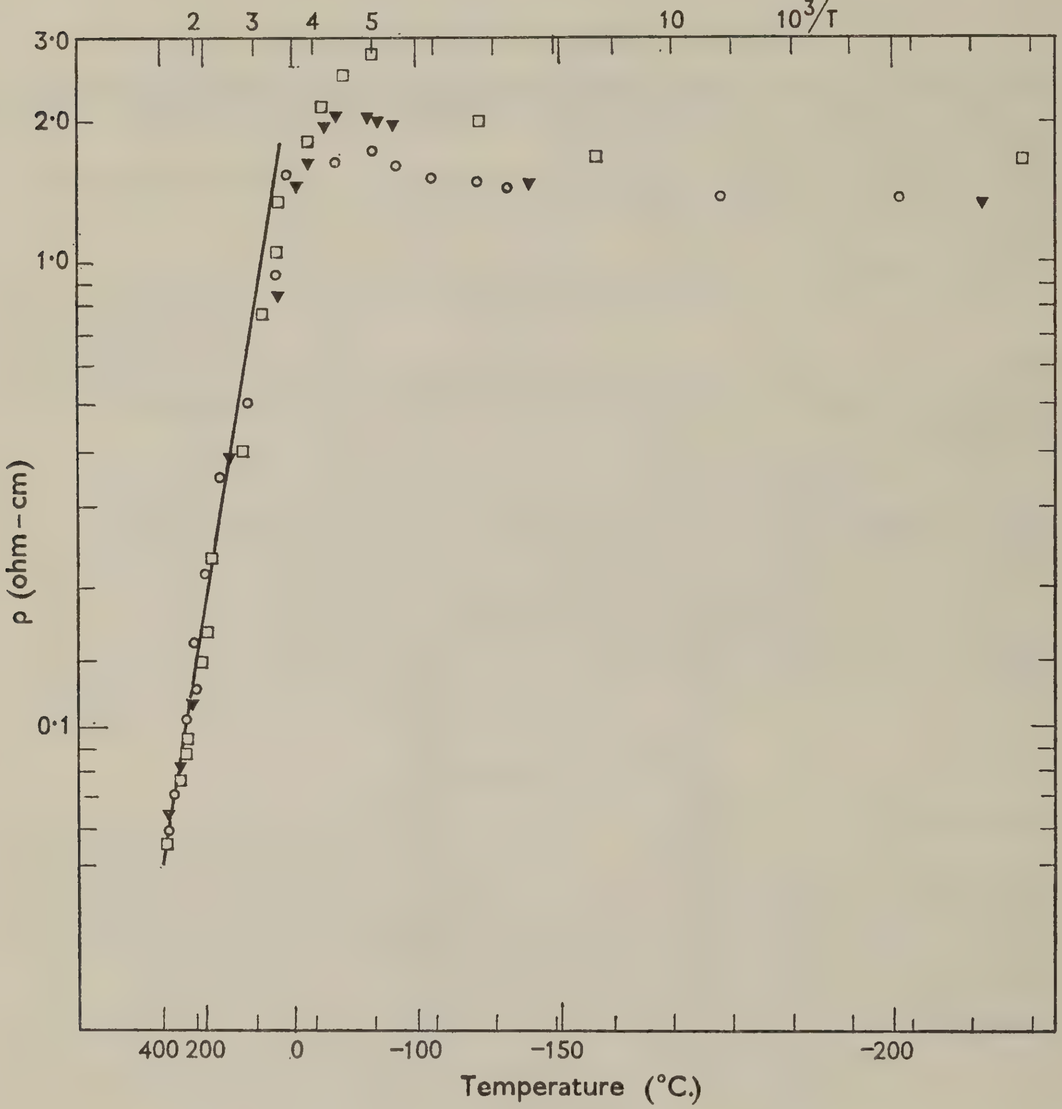


FIG. 12.—The resistivity of three different specimens of black phosphorus as a function of the reciprocal of the temperature in °K.

where $k$ is Boltzmann's constant and $W$ is 0·33 e.v. This is equivalent to

$$\log_{10} \rho = 834T^{-1} - 2{\cdot}523$$

The effect of pressure is shown in Fig. 13.

The Hall constant is shown plotted as a function of temperature in Fig. 14. This constant is independent of the magnetic field up to 5000 gauss. The sign of the Hall voltage indicates that the carriers are positive, a conclusion which is supported by the direction of the thermo-electric effect.

The material used in these measurements was prepared by heating white phosphorus at 200°C. under a pressure of 13,000 kg. cm.$^{-2}$ The volume change in the reaction was 0·18 c.c. g.$^{-1}$

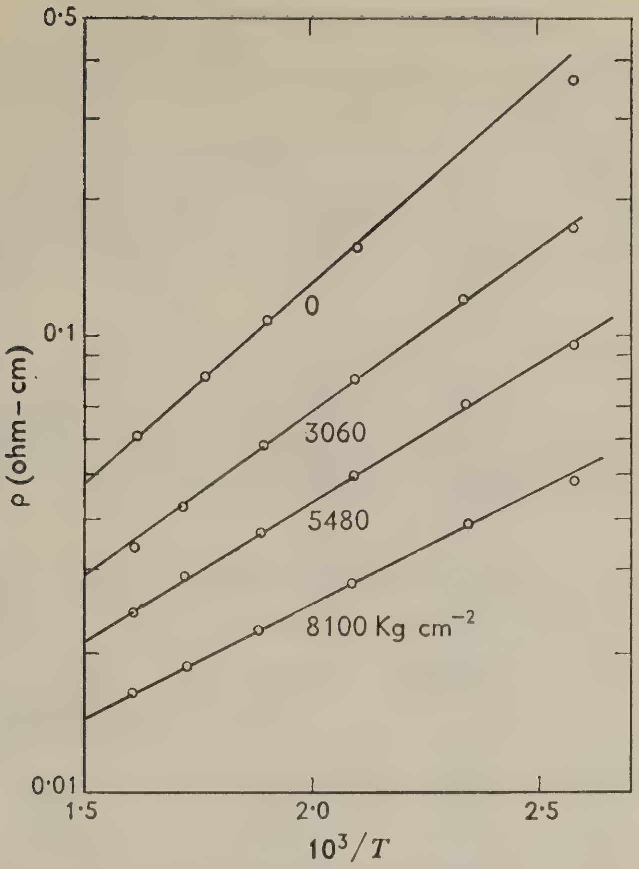


FIG. 13.—Temperature dependence of the resistivity of black phosphorus in the intrinsic range at various pressures

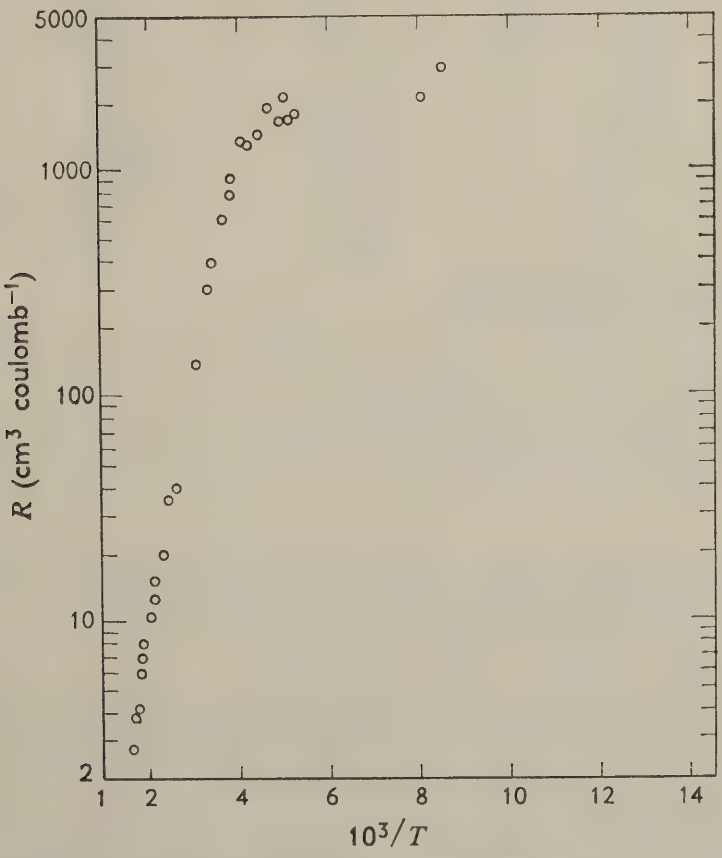


FIG. 14.—The Hall constants ($R$) of several samples of black phosphorus as a function of the reciprocal of the temperature

## THERMODYNAMIC PROPERTIES

Much of the information on the thermal properties of phosphorus is based on experimental data obtained before 1920. In some instances this has been checked by calculations using spectroscopic and other physical data of more recent origin. For the earlier observations the standard state of the element is the α- or cubic form of white phosphorus. In more recent reports,[171–2] however, the reference state for thermodynamic properties is the crystalline, triclinic form (Form V) of red phosphorus.

### Heats of Formation

Data on the heats of formation of various forms of phosphorus as given by the National Bureau of Standards[299] are reproduced in Table XXXI; the values given in column 5 refer to the formula weight indicated in column 3.

*Table XXXI.—Heats of Formation of Phosphorus*[299]

| Form | Temp. (°C.) | Formula | Physical state | Heat of formation (kcal. mole$^{-1}$) | Ref. |
|---|---|---|---|---|---|
| α-White | 25 | $P_4$ | Crystal | 0 | — |
| α-White | 25 | $P_4$ | Liquid | 0·601 | 193 |
| α-White | 25 | $P_4$ | Gas | 13·12 | 182, 191 |
| β-White(a) | −2·4 | $P_4$ | Crystal | −5·40 | 168 |
| Violet | 25 | P | Crystal | −4·4 | 300 |
| Violet(b) | 590 | P | Liquid | 3·85(c)(d) | 168, 169 |
| Violet(b) | 590 | P | Gas | 6·35(c) | 169 |
| Black | 25 | P | Crystal | −10·3 | |
| Monatomic | 25 | P | Gas | 75·18(e) | 68, 73, 74 |
| Diatomic | 25 | $P_2$ | Gas | 33·82(e) | 74, 202, 153 |
| Ion | 25 | $P^+$ | Gas | 329·81 | 59 |
| | 25 | $P^{2+}$ | Gas | 784·51 | 59 |
| | 25 | $P^{3+}$ | Gas | 1481·43 | 59 |
| | 25 | $P^{4+}$ | Gas | 2667·2 | 59 |
| | 25 | $P^{5+}$ | Gas | 4167·9 | 59 |

(a) At a pressure of $4{\cdot}4 \times 10^6$ mm. Hg.
(b) At a pressure of 32,760 mm. Hg.
(c) Heat of formation referred to solid violet phosphorus.
(d) This figure is erroneously given as 4·85 in the National Bureau of Standards Circular 500.[299] See ref. 169, p. 293.
(e) See pages 166, 189, where use of the heat of sublimation of 14 kcal. mole$^{-1}$ $P_4$ for white phosphorus[195] gives $\Delta H_f = 75{\cdot}5$ kcal./g. atom for monatomic gas and 34·25 kcal. mole$^{-1}$ $P_2$ for diatomic gas.

The violet form in Table XXXI is Hittorf's 'metallic' phosphorus, which appears to be identical with triclinic red phosphorus Form V (see page 157). The values given for the ions were calculated from the ionization potentials given in Table II. These data supersede those of Bichowsky and Rossini.[301]

Data on the heat and free energy of formation of phosphorus referred to red phosphorus Form V are summarized in Table XXXII. The heat of formation of red Form V from α-white phosphorus (on which the values in the Table were calculated) is −4·18 kcal. per gram atom. The corresponding free energy is 2·886 kcal./g.-atom, both values being at 25°C.

The reference state for Table XXXII was taken as red, triclinic phosphorus from 298°K. to 704°K. and as ideal diatomic vapour ($P_2$) at higher temperatures.

Table XXXIII gives the corresponding data for solid, cubic, α-white phosphorus.

*Table XXXII.—Heat and Free Energy of Formation of Phosphorus Vapour referred to Red Phosphorus Form V*[171, 172]

| Temp. (°K.) | $\Delta H^\circ_f$ (kcal. mole$^{-1}$) | | | $\Delta G^\circ_f$ (kcal. mole$^{-1}$) | | |
|---|---|---|---|---|---|---|
| | P | $P_2$ | $P_4$ | P | $P_2$ | $P_4$ |
| 298·16 | 79·800 | 42·725 | 30·820 | 69·805 | 30·442 | 17·397 |
| 300 | 79·800 | 42·721 | 30·814 | 69·744 | 30·367 | 17·317 |
| 400 | 79·779 | 42·470 | 30·422 | 66·395 | 26·286 | 12·878 |
| 500 | 79·720 | 42·177 | 29·988 | 63·055 | 22·272 | 8·543 |
| 600 | 79·622 | 41·828 | 29·468 | 59·732 | 18·320 | 4·292 |
| 700 | 79·484 | 41·415 | 28·812 | 56·426 | 14·430 | 0·154 |
| 800 | 58·843 | 0 | −53·830 | 47·843 | 0 | −25·102 |
| 900 | 58·900 | 0 | −53·660 | 46·462 | 0 | −21·512 |
| 1000 | 58·957 | 0 | −53·480 | 45·067 | 0 | −18·000 |
| 1200 | 59·071 | 0 | −53·080 | 42·295 | 0 | −10·864 |
| 1400 | 59·175 | 0 | −52·720 | 39·491 | 0 | −3·888 |
| 1600 | 59·271 | 0 | −52·380 | 36·647 | 0 | +2·996 |
| 1800 | 59·380 | 0 | −52·000 | 33·820 | 0 | +9·938 |
| 2000 | 59·488 | 0 | −51·820 | 30·968 | 0 | +16·770 |
| 2200 | 59·607 | 0 | — | 28·125 | 0 | — |
| 2400 | 59·732 | 0 | — | 25·268 | 0 | — |
| 2600 | 59·888 | 0 | — | 22·370 | 0 | — |
| 2800 | 60·059 | 0 | — | 19·459 | 0 | — |
| 3000 | 60·257 | 0 | — | 16·577 | 0 | — |

*Table XXXIII.—Heat and Free Energy of Formation of Solid α-White Phosphorus*

| Temp. (°K.) | $\Delta H^\circ_f$ (kcal./g. atom) | $\Delta G^\circ_f$ (kcal./g.-atom) |
|---|---|---|
| 298·16 | 4·180 | 2·886 |
| 300 | 4·181 | 2·879 |
| 400 | 4·403 | 2·391 |
| 500 | 4·457 | 1·882 |
| 600 | 4·482 | 1·362 |
| 700 | 4·488 | 0·848 |
| 800 | −16·000 | −4·976 |
| 900 | −15·770 | −3·611 |

### Heat of Atomization

The heat of formation of phosphorus atoms $\frac{1}{4}(\Delta H_1+\Delta H_2+2\Delta H_3)$, has been computed[302] to be 75·3 kcal./g.-atom at 25°C. from the following data:

$$\begin{array}{ll} 4P(g) \rightarrow P_4(g) & \Delta H_1 = 13{\cdot}2 \text{ kcal.} \\ P_4(g) \rightarrow 2P_2(g) & \Delta H_2 = 54{\cdot}5 \text{ kcal.} \\ P_2(g) \rightarrow 2P(g) & \Delta H_3 = 116{\cdot}8 \text{ kcal.} \end{array}$$

$\Delta H_1$ is the heat of sublimation of white phosphorus derived from vapour pressure measurements[182] and $\Delta H_2$ is the value obtained from the dissociation of tetratomic phosphorus vapour.[155, 201] $\Delta H_3$ is based on a spectroscopic dissociation energy of 5·031 e.v. (116·0 kcal. at 0°K.).[75, 203–4] This energy has also been reported to be 5·008 e.v. (115,450 kcal. at 0°K.).[72–4] The higher value is generally accepted as the more reliable.

A more accurate value of the heat of sublimation $\Delta H_1$ is 14·00 kcal./mole $P_4$ at 25°C.[194–5] This yields a value of 75·5 kcal./g. atom for the heat of atomization.

### Heat of Combustion

The heat of formation of the gaseous molecule PO is given as $-9{\cdot}7$ kcal. mole$^{-1}$ at 298·16°K.[76, 299]

The heat of combustion of white phosphorus to form phosphorous oxide, $P_4O_6$, has been reported to be $-486{\cdot}4$[303] and $-538$[300] kcal. per mole of $P_4O_6$. Both of these values appear to be too large and almost certainly refer to a combustion product containing a large proportion of the tetroxide $P_4O_8$. More recent data, based on the oxidation of $P_4O_6$ to $P_4O_{10}$, gives a heat of combustion of phosphorus of $-390$ kcal./mole of $P_4O_6$,[304] giving an enthalpy of formation of $-392$ kcal./mole for the oxide.

The earlier data[301, 305, 299] give the heats of combustion at 298·16°K. of $P_4$ to $P_4O_{10}$ (hexagonal) as $-717$ kcal. mole$^{-1}$ and to amorphous $P_4O_{10}$ as $-731$ kcal. mole.$^{-1}$ More recent determinations give $-710{\cdot}2$ kcal./mole $P_4$ for white phosphorus at 298·16°K. The corresponding data for red phosphorus, form IV, and amorphous red phosphorus are $697{\cdot}7 \pm 0{\cdot}4$ and $703{\cdot}2 \pm 0{\cdot}5$ kcal. mole$^{-1}$ respectively, both values referring to $P_4$ at 298·16°K.[306]

Data on the heat, free energy and entropy have been reported[307–8] for some oxidation reactions of phosphorus. These are summarized in Table XXXIV in the form of the values of the various constants to be used in the equations

$$\begin{aligned}
\Delta H_T &= \Delta H_0 - 10^{-3}bT^2 + 2\times 10^5 cT^{-1}\\
\Delta G_T &= \Delta H_0 + 2{\cdot}303aT\log_{10} T + 10^{-3}bT^2 + 10^5 cT^{-1} + IT\\
\Delta S_T &= -a - 2{\cdot}303a\log_{10} T - 2\times 10^{-3}bT^2 + 10^5 cT^{-2} - I\\
\Delta C_p &= -a - 2\times 10^{-3}bT - 2\times 10^5 cT^{-2}
\end{aligned}$$

*Table XXXIV.—Thermodynamic Data for Some Oxidation Reactions of White Phosphorus*

| Reaction | Temp. (°K.) | $\Delta H_0$ (g.-cal. mole$^{-1}$) | *a* | *b* | *c* | *I* |
|---|---|---|---|---|---|---|
| $P(s)+\frac{1}{2}O_2(g) = PO(g)$ | 298·16–317·4 | −9,370 | +1·10 | — | — | −25·40 |
| $P(l)+\frac{1}{2}O_2(g) = PO(g)$ | 317·4–553 | −9,390 | +1·50 | — | — | −27·63 |
| $P(g)+\frac{1}{2}O_2(g) = PO(g)$ | 553–1500 | −12,640 | +1·00 | — | — | −18·61 |
| $P_4(s)+5O_2(g) = P_4O_{10}(s)$ | 298·16–317·4 | −711,520 | +41·55 | −51·50 | −1·00 | −28·24 |
| $P_4(l)+5O_2(g) = P_4O_{10}(s)$ | 317·4–553 | −711,800 | +42·55 | −51·50 | −1·00 | −33·13 |
| $P_4(g)+5O_2(g) = P_4O_{10}(s)$ | 553–631 | −725,560 | +37·98 | −51·07 | −2·405 | +20·87 |
| $P_4(g)+5O_2(g) = P_4O_{10}(g)$ | 631–1500 | −722,330 | −18·87 | +2·93 | −2·405 | +348·2 |
| $2P(l)+2\frac{1}{2}O_2(g) = P_2O_5(s)$ | 298–631 | −379,000 | — | — | — | 138·4 |
| $2P(g)+2\frac{1}{2}O_2(g) = P_2O_5(g)$ | 631–1400 | −370,000 | — | — | — | 123·3 |

The free energies for $P_2O_5$ and $P_4O_{10}$ calculated from the data in Table XXXIV are not in agreement with one another. This is unavoidable because the entropy of phosphorus pentoxide had not been determined at the time the data were compiled. Later work has given for this entropy[309] a value of $54{\cdot}68 \pm 0{\cdot}1$ g.-cal. deg.$^{-1}$ mole$^{-1}$ for $P_4O_{10}$ at 25°C.

At high temperatures the rate of change of free energy of formation with temperature approaches a constant value. The free energies of formation of some of these reactions have been represented by empirical linear equations. The equations, which are given below, fit the data to within ± 600 g.-cal. per mole of oxide.[306]

$$\begin{array}{lll}
P(l)+\frac{1}{2}O_2(g) = PO(g) & \Delta G_T^\circ = -10{,}000 - 17{\cdot}11T & (298\text{–}553^\circ\text{K.})\\
P(g)+\frac{1}{2}O_2(g) = PO(g) & \Delta G_T^\circ = -13{,}500 - 10{\cdot}73T & (553\text{–}1500^\circ\text{K.})\\
P_4(l)+5O_2(g) = P_4O_{10}(s) & \Delta G_T^\circ = -722{,}530 + 227{\cdot}11T & (298\text{–}553^\circ\text{K.})\\
P_4(g)+5O_2(g) = P_4O_{10}(s) & \Delta G_T^\circ = -722{,}530 + 227{\cdot}11T & (553\text{–}631^\circ\text{K.})\\
P_4(g)+5O_2(g) = P_4O_{10}(g) & \Delta G_T^\circ = -707{,}490 + 205{\cdot}02T & (631\text{–}1500^\circ\text{K.})
\end{array}$$

Owing to their empirical nature, these equations are not suitable for calculating the entropy or heat of formation at any particular temperature.

## Latent Heat of Fusion

$\alpha$-White phosphorus has a latent heat of fusion of 601 g.-cal./mole $P_4$ at the melting point (44·2°C.). The variation with temperature is given by the equation[192]

$$L_{t^\circ\text{C.}} = 506+3{\cdot}02t-19{\cdot}121\times10^{-3}t^2-1{\cdot}309\times10^{-5}t^3 \text{ g.-cal./mole } P_4$$
$$t = 0^\circ \text{ to } 100^\circ\text{C.}$$

The effect of pressure on the latent heat of fusion ($\lambda$) is reported to be given by the equation

$$\frac{\mathrm{d}\lambda}{\mathrm{d}p} = \frac{\mathrm{d}T}{\mathrm{d}p}(C_1-C_s)+\delta V-T\left[\left(\frac{\partial V_e}{\partial T}\right)_p - \left(\frac{\partial V_s}{\partial T}\right)_p\right]$$

where $C_1$ and $C_s$ are the specific heats of liquid and solid phosphorus, $\delta V$ is the change in volume on melting and $V_e$ and $V_s$ are the specific volumes of the liquid and solid states.[310]

It has been pointed out that the entropy of fusion of white phosphorus (i.e. the molar heat of fusion of $P_4$ in calories divided by the melting point on the absolute scale of temperature) is very nearly equal to the gas constant $\boldsymbol{R}$.[311, 312] This has been interpreted as indicating no new degree of freedom between the atoms of the molecule in the liquid state.[312]

The latent heat of fusion of violet phosphorus (red phosphorus form V) is given as 15·6 kcal./mole $P_4$ at 590°C.[169] This high value is not a true heat of fusion, because violet phosphorus on melting changes to liquid white phosphorus containing $P_4$ molecules. The observed heat therefore includes the heat of depolymerization and other transitions which occur on melting. It should be noted that the latent heat of fusion has been incorrectly reported as 19·4 kcal./mole $P_4$.[299]

No value appears to have been reported for the latent heat of fusion of crystalline black phosphorus. However, the heat of sublimation at 580°C. is 33·6 ± 2 kcal./mole $P_4$.[170] By subtracting from this 10·6 kcal./mole $P_4$ for the heat of vaporization of liquid phosphorus at 580°C.,[169] the approximate value of 23 ± 2 kcal./mole $P_4$ is obtained for the latent heat of fusion.

## Latent Heat of Vaporization

Data on the latent heat of vaporization of liquid white phosphorus are derived from vapour pressure measurements. There is some variation in the values given in the literature, and the best figure seems to be 13·47 kcal./mole $P_4$ at 25°C.[171–2] This is derived from the latent heat of fusion (0·57 kcal./mole $P_4$ calculated as $L_{25^\circ\text{C.}}$ from the equation given above) and the heat of sublimation at 25°C. (14·0 ± 0·3 kcal./mole $P_4$).[194–5] The variation in the reported values has already been discussed (see pages 164–166).

In the temperature range 317° to 629°K. the latent heat is given by the equation[155]

$$\Delta H^\circ = 14{,}714-7{\cdot}7603T+4{\cdot}9122\times10^{-3}T^2 \text{g.-cal. mole } P_4$$

This equation is derived from the earlier vapour pressure measurements[145, 182, 185] and slight modifications are necessary to take account of more recent observations.[194–5] The values of the latent heat of vaporization calculated from this equation are 12·84 kcal./mole $P_4$ at 25°C. and 11·92 kcal./mole $P_4$ at the boiling point (280·5°C.). The corresponding values given by the Bureau of Standards are 12·62 and 11·88 kcal./mole $P_4$, respectively.[299]

The latent heat of vaporization of violet phosphorus has been reported as 10·2 kcal./mole $P_4$ at 590°C.[169] It is probable that this is actually the heat of vaporization of liquid white phosphorus.

## Heats of Transition

Several measurements have been made of the heat changes involved in the transitions between the various forms of phosphorus. The data are summarized in Table XXXV.

The accuracy of some of these data is uncertain,[306] and from an examination of the heats of transition it has been suggested[195] that the calorimetric data may be in error.

The heats of transition of white phosphorus to red, crystalline black and amorphous black phosphorus are derived from the heats of reaction of the appropriate allotropes with bromine in carbon disulphide.[164] These values (−69, −91 and −62 kcal./mole $P_4$, respectively, at 20°C.) appear to be much too large. However, the data were calculated on the assumption that the red and black phosphorus had formed phosphorus pentabromide on bromination. The heats of reaction were compared with previous data[315–16] on the bromination of white phosphorus to form phosphorus pentabromide. If in fact the red and black forms gave the tribromide, and the heat of formation of the latter from white phosphorus and bromine in carbon disulphide solution is taken to be 47·5 kcal./mole $PBr_3$,[155, 299] the above values become −21, −44 and −14 kcal./mole $P_4$, respectively.

*Table XXXV.—Heats of Transition of Phosphorus Allotropes*

| Initial form | Final form | Temp. (°C.) | $\Delta H$ transition (kcal./mole $P_4$) | Ref. |
|---|---|---|---|---|
| α-White | β-White | −76·9 | −3·8±0·2 | 133, 195 |
| α-White | Violet | 25 | −16·6±0·8 | 195, 313, 314 |
| α-White | Red amorphous | 25 | −7·0±1·1 | 306 |
| α-White | Red form IV | 25 | −12·5±1·1 | 306 |
| α-White | Black (cryst.) | 25 | −24·7±2·3 | 195 |
| Violet | Black (cryst.) | 25 | −8·1±2·5 | 195 |
| Red | Black (cryst.) | 350 | −18·2 | 133, 164, 183 |
| Black (amorph.) | Black (cryst.) | 20 | Approx. −30 | 164 |

## Heats of Sublimation

Data on the heats of sublimation of phosphorus allotropes are given in Table XXXVI. The values are referred to the $P_4$ molecule irrespective of the vapour phase shown in column 2; hence, in order to obtain values for $P_2$ and P the figures should be divided by two and four, respectively.

*Table XXXVI.—Heats of Sublimation of Phosphorus*

| Form | Vapour phase | Temp. (°C.) | $\Delta H$ sublimation (kcal./mole $P_4$) | Ref. |
|---|---|---|---|---|
| α-White | $P_4$ | 25 | 14·0±0·3 | 194, 195 |
| α-White | $P_2$ | 25 | 68·5 | 171, 172 |
| α-White | P | 25 | 302·5* | 171, 172 |
| Violet | $P_4$ | 25 | 30·6±0·5 | 169, 195 |
| Violet | $P_4$ | 360–590 | 25·9 | 155 |
| Violet | $P_4$ | 413 | 25·6±2·5 | 317 |
| Red form I | $P_4$ | 320–500 | 19·7 | 155 |
| Red form II | $P_4$ | 310–500 | 24 | 155 |
| Red form IV | $P_4$ | 380–560 | 28 | 155 |
| Red form V | $P_4$ | 320–510 | 28·8 | 155 |
| Red form V | $P_4$ | 25 | 30·8 | 171 |
| Red form V | $P_2$ | 25 | 85·5 | 171, 172 |
| Red form V | P | 25 | 319 | 171, 172 |
| Black (cryst.) | $P_4$ | 25 | 38·7±2·0 | 195 |
| Black (cryst.) | $P_4$ | 453 | 33·1±2·5 | 133, 317 |
| Black (cryst.) | $P_4$ | 552–578 | 33·6±2·0 | 170 |

* Based on $\Delta H = 14{\cdot}0$ for α-white phosphorus.

The values reported for white phosphorus have already been discussed (see pages 164–166). There are some differences in the data given for red phosphorus and it should be noted that the heats of sublimation for forms I to V are average values derived from vapour pressure equations. Except for form V it is possible that heating may have caused changes in the phosphorus which have an effect on its vapour pressure.[155]

The heat of sublimation at 25°C. for violet phosphorus is a value calculated from high temperature vapour pressure data,[169] and corrected to 25°C. using published values[318] for the heat capacities of phosphorus vapour and solid red phosphorus. The heat of sublimation of black phosphorus is obtained in a similar manner, also using the heat capacity data for solid red phosphorus. The latter are considered to be a sufficiently good approximation in the absence of experimental heat capacity values for black phosphorus.[195]

The heat of sublimation of $\alpha$-white phosphorus to monatomic vapour has been calculated to be $292{\cdot}6 \pm 8$ kcal./mole $P_4$.[319] An earlier calculated value of 424 kcal./mole $P_4$ seems to be too large.[320]

The value of 79 kcal./mole $P_4$ reported[319] for the sublimation of red phosphorus to diatomic vapour agrees with that given in Table XXXV when it is corrected for the more recent and more accurate values of the separate heats used in the earlier calculation.

## Atomic and Specific Heats

The atomic heat of solid white phosphorus at 25°C. has been given as 5·55,[299] 5·62[318] and 5·69[321] g.-cal./g. atom. The values given for liquid white phosphorus at 44·1°C. are 5·88,[318] 6·05[299, 322] and 6·24[321] g.-cal./g.atom.

The value of the expression $A/\alpha T_m$, where $A$ is the atomic heat, $\alpha$ the coefficient of cubical expansion and $T_m$ is the melting point in °K., is reported to be 48 g.-cal. deg.$^{-1}$ for solid white phosphorus and 36 g.-cal. deg.$^{-1}$ for the liquid.[323]

The molar specific heat of solid white phosphorus has been calculated by considering the unit cell to consist of $P_4$ molecules having a total of 48 degrees of freedom. Of these, 24 were identified with the internal vibrations of the $P_4$ molecule as specified by the observed Raman frequencies and their degeneracies, 12 were associated with the inactive frequency of a triply degenerate oscillation of each of four $P_4$ molecules, and 9 were associated with the observed low-frequency vibration due to hindered translations of $P_4$ molecules in the unit cell; this low-frequency was taken to be 36 cm.$^{-1}$ and the three hindered rotations of the $P_4$ molecules were assumed to correspond to a frequency of 67 cm.$^{-1}$ The remaining three degrees of freedom were considered to be due to simple translations of the unit cell.[324] In the assignment of the observed Raman frequencies, the 606 cm.$^{-1}$ frequency is identified as single and due to the symmetrical vibration, the 363 cm.$^{-1}$ is doubly degenerate and the 465 cm.$^{-1}$ one is triply degenerate.[69, 70] From these data the following equation expressed in Einstein terms was derived for the molar specific heat at constant volume

$$C_v = \tfrac{1}{4}E(\theta_{36}/T)+\tfrac{3}{4}E(\theta_{36}/T)+E(\theta_{67}/T)+\tfrac{1}{3}E(\theta_{606}/T)+\tfrac{2}{3}E(\theta_{363}/T)+E(\theta_{465}/T)$$

The difference in specific heats, $C_p - C_v$, at room temperature was calculated from thermodynamic data to be 3·06. At other temperatures Gruneisen's law[325]

$$C_p - C_v = \alpha^2 VT/\beta$$

where $\alpha$ = coefficient of cubical expansion, $\beta$ = coefficient of compressibility, $V$ = specific volume, was used. Since $\alpha$ is proportional to $C_v$ and the specific volume and compressibility vary little with temperature,

$$C_p - C_v = A\, C_v^2\, T$$

In this expression, $A$ is a constant which can be calculated from a known value of $C_p - C_v$ and the value of $C_v$ at 300°K.

The values of $C_p$ found in this way are compared in Table XXXVII with the mean specific heat data found by Dewar[326] at 50°K. and by Ewald[327] at 82° to 290°K. In this Table $U = E(\theta/T)$.

*Table XXXVII.—The Calculated Mean Molar Specific Heat of White Phosphorus (in* g.*-cal./mole* $P_4$*) at* 23° *to* 290°K.

| Parameter | Temperature—°K. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 23 | 77 | 82 | 194 | 195 | 271 | 274 | 290 |
| $\frac{1}{4}U_{36}$ | 9 | 80 | 87 | 251 | 253 | 366 | 371 | 395 |
| $\frac{3}{4}U_{36}$ | 27·4 | 241·5 | 262·9 | 754·5 | 760·5 | 1099·5 | 1113 | 1185 |
| $U_{67}$ | 8·9 | 230·2 | 256·6 | 894·7 | 898·6 | 1345 | 1362 | 1456 |
| $\frac{1}{3}U_{606}+\frac{2}{3}U_{363}+U_{465}$ | 0 | 3·2 | 5·0 | 305·4 | 310·7 | 801·9 | 824·5 | 948·6 |
| $U$ (total) | 45·3 | 555 | 612 | 2206 | 2223 | 3612 | 3670 | 3984 |
| Mean $C_v$ $= (U_2-U_1)/(T_2-T_1)$ | 9·45 | | 14·23 | | 18·28 | | 19·63 | |
| $C_p-C_v$ | 0·10 | | 0·78 | | 2·34 | | 3·06 | |
| Mean $C_p$ (calculated) | 9·55 | | 15·01 | | 20·62 | | 22·69 | |
| Mean $C_p$ (observed) | 9·60 | | 15·44 | | 20·48 | | 22·0 | |

## Heat Capacity

The molar heat capacity of solid white phosphorus between 273·16°K. and 317·26°K. is given by the expression

$$C_p = 13{\cdot}615 + 28{\cdot}72 \times 10^{-3}T \text{ g.-cal. (mole P}_4)^{-1} \text{ deg.}^{-1}$$

This gives molar heat capacities of 22·18 and 22·73 at 25° and 44·2°C., respectively.[192]

For liquid and supercooled white phosphorus the molar heat capacity equation is

$$C_p = 24{\cdot}151 + 11{\cdot}932 \times 10^{-3}T - 3{\cdot}927 \times 10^{-5}T^2 \text{ g.-cal. (mole P}_4)^{-1} \text{ deg.}^{-1}$$

which represents measurements made between 298·16° and 370·16°K.[192]

Calculations by separate thermodynamic paths of the free energy of vaporization of white phosphorus indicate that the above heat capacity equation for liquid phosphorus is probably reliable up to 623·16°K.[155] (see, however, page 203).

The molar heat capacity of tetratomic phosphorus vapour is closely represented between 298° and 1500°K. by[155, 191]

$$C_p = 19{\cdot}227 + 0{\cdot}509 \times 10^{-3}T - 2{\cdot}975 \times 10^{5}T^{-2} \text{ g.-cal. (mole P}_4)^{-1} \text{ deg.}^{-1}$$

This equation is derived from values of the heat content $H_T^\circ - H_0^\circ$ obtained by a statistical mechanical calculation.[77]

For diatomic phosphorus vapour the molar heat capacity between 298° and 2000°K. is represented to within 0·02 g.-cal. by the equation

$$C_p = 6{\cdot}9545 + E(1114/T) + 5{\cdot}84 \times 10^{-5}T$$

where $E$ is the Einstein function corresponding to a vibration frequency of 778 cm.$^{-1}$ ($E = x^2e^x/(e^x-1)^2$ where $x$ is $1114/T$).[328–9] This is equivalent to

$$C_p = 8{\cdot}86 + 0{\cdot}08 \times 10^{-3}T - 1{\cdot}20 \times 10^{5}T^{-1}$$

Two other equations which represent the data[65, 172] less closely are[191]:

$$C_p = 8{\cdot}643 + 0{\cdot}202 \times 10^{-3}T - 1{\cdot}03 \times 10^{5}T^{-2}$$

and[155]

$$C_p = 8{\cdot}44 + 0{\cdot}38 \times 10^{-3}T - 0{\cdot}836 \times 10^{5}T^{-2}$$

The heat capacity of monatomic phosphorus vapour is constant at 4·97 g.-cal./g.atom P up to 1500°K. It increases to 5·06 at 2000°K. and 5·62 at 3000°K. (see page 196, Table XXXIX).[65, 172]

In the temperature range 300° to 1500°K. the molar heat capacities of diatomic and tetratomic phosphorus vapour at constant volume are represented by the equations[320]:

$$P_2:\quad C_v = 4{\cdot}04 + 7{\cdot}17 \times 10^{-3}T - 6{\cdot}3 \times 10^{-6}T^2 + 1{\cdot}85 \times 10^{-9}T^3$$
$$P_4:\quad C_v = 8{\cdot}33 + 25{\cdot}9 \times 10^{-3}T - 24{\cdot}2 \times 10^{-6}T^2 + 7{\cdot}41 \times 10^{-9}T^3$$

The data available on the heat capacity of red phosphorus appear to be rather less precise than those for the white modification. The earlier measurements[327, 330] are represented to within ±10% between 273° and 473°K. by the equation[322]

$$C_p = 0{\cdot}21 + 18 \times 10^{-3}T \text{ g.-cal./mole P}$$

The data are not considered to be reliable enough for thermochemical calculations.[331] Measurements[332] of the mean specific heat between 295·16 and 873·16°K. give the following molar heat capacity equation[322] in g.-cal./g.atom

$$C_p = 2{\cdot}67 + 7{\cdot}8 \times 10^{-3}T; \qquad T = 573° \text{ to } 773°\text{K.}$$

This agrees fairly well with the specific heat obtained by Regnault (Mellor, VIII, 760).

### Heat Content, Free Energy and Entropy

From a critical examination of the information available up to 1948, Kelley[318, 333] compiled data on the heat content and entropy of phosphorus. These are summarized in Table XXXVIII which gives the values of the constants to be used in the equations which follow. The data refer to calories per mole of the species indicated in column 2 of the Table.

$$\begin{aligned} C_p &= a + b \times 10^{-3}T + c \times 10^5 T^{-2} \\ H_T - H_{298} &= aT + \tfrac{1}{2}b \times 10^{-3}T^2 - c \times 10^5 T^{-1} - d \\ S_T - S_{298} &= 2{\cdot}303a \log_{10} T + b \times 10^{-3}T - \tfrac{1}{2}c \times 10^5 T^{-2} - e \end{aligned}$$

*Table XXXVIII.—Heat Content and Entropy of Phosphorus*

| Form | Formula | Temp. (°K.) | *a* | *b* | *c* | *d* | *e* | Relative Accuracy (%) | $S_{298}$ |
|---|---|---|---|---|---|---|---|---|---|
| White (liquid) | $P_4$ | 317–400 | 23·5 | 0·8 | — | 6425 | 132·4 | 1 | 44·4 |
| Red (solid) | P | 298–800 | 4·74 | 3·9 | — | 1587 | 28·12 | 5 | 7·4 |
| Ideal gas | P | 298–1500 | 4·97 | — | — | 1482 | 28·33 | 0·1 | 38·99 |
| Ideal gas | $P_2$ | 298–2000 | 8·31 | 0·46 | −0·72 | 2740 | 47·91 | 0·5 | 52·11 |
| Ideal gas | $P_4$ | 298–1500 | 18·93 | 0·86 | −2·81 | 6625 | 109·7 | 1 | 66·85 |

It should be noted that these are empirical equations. Although they represent the data within the accuracy stated, the equations must not be confused with those quoted elsewhere (e.g., page 194) which are derived by statistical mechanical methods or are based on calculations from spectroscopic data.

A more recent survey[334, 335] gives the same data, except for the entropy of liquid white phosphorus for which the value $S_{298} = 41{\cdot}2$ is considered to be more accurate. It has been shown experimentally that the enthalpy of liquid phosphorus varies in a smooth and continuous fashion from −1°C. through the melting point at 44°C.[479] It shows no anomaly near the melting point, such as would be associated with the changes in molecular association postulated by previous authors on the basis of the viscosity behaviour of supercooled liquid phosphorus.[231–2, 230]

Table XXXIX.—Thermodynamic Properties of Phosphorus Vapour[171]

| Temp. (°K.) | P—ideal gas (g.-cal./g. atom) | | | | $P_2$—ideal gas (g.-cal./mole) | | | | $P_4$—ideal gas (g.-cal./mole) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_p^\circ$ | $H_T^\circ - H_{298}^\circ$ | $S_T^\circ$ | $-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$ | $C_p^\circ$ | $H_T^\circ - H_{298}^\circ$ | $S_T^\circ$ | $-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$ | $C_p^\circ$ | $H_T^\circ - H_{298}^\circ$ | $S_T^\circ$ | $-\left(\frac{G^\circ - H_{298}^\circ}{T}\right)$ |
| 298·15 | 4·97 | 0 | 38·98 | 38·98 | 7·65 | 0 | 52·11 | 52·11 | 16·05 | 0 | 66·85 | 66·85 |
| 300 | 4·97 | 9 | 39·01 | 38·98 | 7·66 | 14 | 52·16 | 52·12 | 16·06 | 30 | 66·95 | 66·85 |
| 400 | 4·97 | 506 | 40·44 | 39·18 | 8·04 | 799 | 54·42 | 52·43 | 17·51 | 1710 | 71·78 | 67·51 |
| 500 | 4·97 | 1003 | 41·55 | 39·55 | 8·30 | 1618 | 56·25 | 53·02 | 18·28 | 3500 | 75·77 | 68·77 |
| 600 | 4·97 | 1500 | 42·45 | 39·95 | 8·48 | 2459 | 57·78 | 53·69 | 18·73 | 5360 | 79·16 | 70·23 |
| 700 | 4·97 | 1996 | 43·22 | 40·37 | 8·60 | 3314 | 59·11 | 54·38 | 19·02 | 7240 | 82·06 | 71·72 |
| 800 | 4·97 | 2493 | 43·88 | 40·77 | 8·68 | 4179 | 60·26 | 55·04 | 19·21 | 9150 | 84·61 | 73·18 |
| 900 | 4·97 | 2990 | 44·47 | 41·15 | 8·74 | 5052 | 61·29 | 55·68 | 19·35 | 11080 | 86·88 | 74·57 |
| 1000 | 4·97 | 3487 | 44·99 | 41·51 | 8·79 | 5930 | 62·20 | 56·27 | 19·44 | 13020 | 88·92 | 75·90 |
| 1100 | 4·97 | 3984 | 45·47 | 41·85 | 8·83 | 6812 | 63·05 | 56·86 | 19·52 | 14980 | 90·79 | 77·18 |
| 1200 | 4·97 | 4481 | 45·90 | 42·17 | 8·86 | 7698 | 63·83 | 57·42 | 19·57 | 16940 | 92·50 | 78·39 |
| 1300 | 4·97 | 4978 | 46·30 | 42·48 | 8·88 | 8586 | 64·53 | 57·93 | 19·62 | 18900 | 94·06 | 79·53 |
| 1400 | 4·97 | 5475 | 46·66 | 42·75 | 8·91 | 9477 | 65·19 | 58·43 | 19·65 | 20860 | 95·52 | 80·62 |
| 1500 | 4·98 | 5972 | 47·01 | 43·03 | 8·93 | 10370 | 65·81 | 58·90 | 19·68 | 22830 | 96·88 | 81·66 |
| 1600 | 4·99 | 6471 | 47·33 | 43·29 | 8·94 | 11265 | 66·38 | 59·34 | 19·70 | 24800 | 98·15 | 82·65 |
| 1700 | 5·00 | 6970 | 47·63 | 43·53 | 8·96 | 12161 | 66·92 | 59·77 | 19·72 | 26770 | 99·35 | 83·61 |
| 1800 | 5·01 | 7470 | 47·92 | 43·77 | 8·97 | 13059 | 67·44 | 60·19 | 19·74 | 28740 | 100·47 | 84·51 |
| 1900 | 5·04 | 7973 | 48·19 | 44·00 | 8·99 | 13958 | 67·92 | 60·58 | 19·75 | 30720 | 101·54 | 85·38 |
| 2000 | 5·06 | 8478 | 48·45 | 44·22 | 9·00 | 14858 | 68·38 | 60·96 | 19·76 | 32690 | 102·55 | 86·21 |
| 2100 | 5·09 | 8985 | 48·70 | 44·43 | 9·01 | 15760 | 68·82 | 61·32 | | | | |
| 2200 | 5·13 | 9497 | 48·93 | 44·62 | 9·02 | 16661 | 69·24 | 61·67 | | | | |
| 2300 | 5·18 | 10012 | 49·16 | 44·81 | 9·03 | 17565 | 69·64 | 62·01 | | | | |
| 2400 | 5·22 | 10532 | 49·38 | 45·00 | 9·04 | 18468 | 70·03 | 62·34 | | | | |
| 2500 | 5·28 | 11057 | 49·60 | 45·18 | 9·05 | 19373 | 70·40 | 62·66 | | | | |
| 2600 | 5·34 | 11588 | 49·81 | 45·36 | 9·05 | 20280 | 70·75 | 62·95 | | | | |
| 2700 | 5·40 | 12125 | 50·01 | 45·52 | 9·06 | 21186 | 71·09 | 63·25 | | | | |
| 2800 | 5·47 | 12669 | 50·21 | 45·69 | 9·07 | 22090 | 71·42 | 63·54 | | | | |
| 2900 | 5·54 | 13219 | 50·40 | 45·85 | 9·08 | 23000 | 71·74 | 63·81 | | | | |
| 3000 | 5·62 | 13777 | 50·59 | 46·00 | 9·09 | 23910 | 72·05 | 64·08 | | | | |
| $H_{298\cdot15}^\circ - H_0^\circ$ | 1481 | | | | 2133 | | | | 3368 | | | |

Expressions for the heat content have been derived[155] from the heat capacity equations given above (pages 194–195) for diatomic and tetratomic phosphorus vapour. These are[155]

$$P_2:\quad H^\circ - H^\circ_0 = -678 + 8{\cdot}44T + 0{\cdot}19\times10^{-3}T^2 + 0{\cdot}836\times10^5T^{-1}\,\text{g.-cal. mole}^{-1}$$
$$P_4:\quad H^\circ - H^\circ_0 = -3380 + 19{\cdot}23T + 0{\cdot}255\times10^{-3}T^2 + 2{\cdot}980\times10^5T^{-1}\,\text{g.-cal. mole}^{-1}$$

The entropy at 298·16°K. of solid α-white phosphorus has been given as 10·6 ± 0·5 g.-cal.(g.atom)$^{-1}$ deg.$^{-1}$ [333] and 9·8 g.-cal.(g.atom)$^{-1}$ deg.$^{-1}$ [172, 334]; the second is regarded as the better value.[334] The corresponding data for crystalline violet and crystalline black phosphorus are 7·4 ± 0·5 and 5·3 ± 0·5 g.-cal.(g. atom)$^{-1}$ deg.$^{-1}$ [333] A later determination of the heat capacity of black phosphorus from 13·0 to 293·8°K. gave values of $S^\circ_{298{\cdot}15} = 5{\cdot}457 \pm 0{\cdot}010$ g.-cal./g. atom/deg. and $H_{298{\cdot}15} - H^\circ_0 = 882{\cdot}6 \pm 1{\cdot}5$ g.-cal./g. atom, in good agreement with previous work.[480]

Thermodynamic properties referred to triclinic red phosphorus form V have been reported[171] for temperatures up to 3000°K. These data, which are given in Table XXXIX and Table XL, were compiled[172] from the heat capacities given by Kelley[318] in conjunction with other relevant information.[155, 336]

*Table XL.—Thermodynamic Properties of Triclinic Red Phosphorus and Cubic α-White Phosphorus*

| Temp. (°K.) | Red, triclinic (g.-cal./g. atom) | | | | α-White, cubic solid (g.-cal./g. atom) | | | |
|---|---|---|---|---|---|---|---|---|
| | $C^\circ_p$ | $H^\circ_T - H_{298}$ | $S^\circ_T$ | $-\left(\frac{G^\circ - H_{298}}{T}\right)$ | $C^\circ_p$ | $H^\circ_T - H_{298}$ | $S^\circ_T$ | $-\left(\frac{G^\circ - H_{298}}{T}\right)$ |
| 298·15 | 4·98 | 0 | 5·46 | 5·46 | 5·63 | 0 | 9·80 | 9·80 |
| 300 | 4·98 | 9 | 5·49 | 5·46 | 5·63 | 10 | 9·83 | 9·80 |
| 400 | 5·37 | 527 | 6·98 | 5·67 | 6·00 | 750 | 12·01 | 10·14 |
| 500 | 5·76 | 1083 | 8·22 | 6·06 | 6·15 | 1360 | 13·37 | 10·65 |
| 600 | 6·14 | 1678 | 9·30 | 6·51 | 6·30 | 1980 | 14·50 | 11·20 |
| 700 | 6·53 | 2312 | 10·28 | 6·98 | 6·45 | 2620 | 15·48 | 11·74 |
| 800 | 4·34 | 23,450 | 30·13 | 0·82 | 6·60 | 3270 | 16·35 | 12·27 |
| 900 | 4·37 | 23,890 | 30·65 | 4·11 | 6·75 | 3940 | 17·14 | 12·77 |
| 1000 | 4·40 | 24,330 | 31·10 | 6·77 | | | | |
| 1100 | 4·42 | 24,770 | 31·53 | 9·02 | | | | |
| 1200 | 4·43 | 25,210 | 31·92 | 10·92 | | | | |
| 1300 | 4·44 | 25,660 | 32·27 | 12·54 | | | | |
| 1400 | 4·46 | 26,100 | 32·60 | 13·96 | | | | |
| 1500 | 4·47 | 26,550 | 32·91 | 15·21 | | | | |
| 1600 | 4·47 | 27,000 | 33·19 | 16·32 | | | | |
| 1700 | 4·48 | 27,440 | 33·46 | 17·32 | | | | |
| 1800 | 4·49 | 27,890 | 33·72 | 18·23 | | | | |
| 1900 | 4·50 | 28,340 | 33·96 | 19·05 | | | | |
| 2000 | 4·50 | 28,790 | 34·19 | 19·80 | | | | |
| 2100 | 4·51 | 29,240 | 34·41 | 20·49 | | | | |
| 2200 | 4·51 | 29,690 | 34·62 | 21·13 | | | | |
| 2300 | 4·52 | 30,150 | 34·82 | 21·72 | | | | |
| 2400 | 4·52 | 30,600 | 35·02 | 22·27 | | | | |
| 2500 | 4·53 | 31,050 | 35·20 | 22·78 | | | | |
| 2600 | 4·53 | 31,500 | 35·38 | 23·27 | | | | |
| 2700 | 4·53 | 31,950 | 35·55 | 23·72 | | | | |
| 2800 | 4·54 | 32,410 | 35·71 | 24·14 | | | | |
| 2900 | 4·54 | 32,860 | 35·87 | 24·54 | | | | |
| 3000 | 4·54 | 33,320 | 36·03 | 24·93 | | | | |

The reference state for the above Tables is red triclinic phosphorus from 298° to 704°K. and ideal gas above this. The following additional enthalpy data were used in compiling the tables:

Heat of sublimation of red phosphorus to $P_4$ = 30·82 kcal./mole $P_4$ at 298°K.
Sublimation of red phosphorus to $P_2$ gas = 42·725 kcal./mole $P_2$ at 298°K.
$\left\{\begin{array}{l}\text{Dissociation } P_4 \rightarrow 2P_2 = 54{\cdot}630 \text{ kcal./mole } P_4 \text{ at } 298^\circ\text{K.}\\ \text{Dissociation } P_2 \rightarrow P \text{ gas} = 116{\cdot}0 \text{ kcal./mole } P_2 \text{ at } 0^\circ\text{K.}\end{array}\right.$
Sublimation of red to P gas = 79·5 kcal./g. atom at 298°K.

Heat of sublimation of red phosphorus to $P_4$ at 704°K. = 7·2 kcal./g. atom.
Heat of sublimation of α-white phosphorus to $P_4$ = 14·1 kcal./mole $P_4$ at 298°K.
Heat of vaporization of liquid white phosphorus = 2·960 kcal./g. atom at 554°K.
Formation of α-white phosphorus from red phosphorus = 4·18 kcal./g. atom at 298°K.

It should be noted that in one compilation[77] of the free energy functions of monatomic phosphorus vapour, the entropy values are all too low by 3·4 g.-cal./g.-atom/deg.

Thermodynamic functions of phosphorus vapour as ideal gas at one atmosphere pressure, without nuclear spin effects, have been calculated[337] using an I.B.M. 704 digital computer. The results for monatomic and diatomic phosphorus vapours up to 3000°K. agree to within one in the second place of decimals with the values given in Table XXXIX and Table XL. The data for temperatures above 3000°K. are given in Table XLI in which the data agree with other and simplified calculations,[338] when allowance is made for changes in the values of fundamental constants and approximations made in the previous calculation.[338]

*Table XLI.—Thermodynamic Functions of* $P(g)$ *and* $P_2(g)$ *in the Ideal Gas State*
(All entropy data in g.-cal. mole$^{-1}$ deg.$^{-1}$)

| Temp. (°K.) | $P(g)$ | | | $P_2(g)$ | | |
|---|---|---|---|---|---|---|
| | $C_p^\circ$ | $S^\circ$ | $-\left(\frac{G^\circ-H_0^\circ}{T}\right)$ | $C_p^\circ$ | $S^\circ$ | $-\left(\frac{G^\circ-H_0^\circ}{T}\right)$ |
| 273·15 | 4·968 | 38·544 | 33·576 | 7·540 | 51·442 | 44·346 |
| 298·15 | 4·968 | 38·977 | 34·011 | 7·656 | 52·108 | 44·970 |
| 3000 | 5·617 | 50·588 | 45·502 | 9·074 | 72·038 | 63·365 |
| 3100 | 5·693 | 50·774 | 45·669 | 9·080 | 72·335 | 63·650 |
| 3200 | 5·771 | 50·956 | 45·832 | 9·086 | 72·624 | 63·926 |
| 3300 | 5·851 | 51·134 | 45·990 | 9·092 | 72·903 | 64·193 |
| 3400 | 5·931 | 51·310 | 46·143 | 9·098 | 73·175 | 64·454 |
| 3500 | 6·010 | 51·483 | 46·294 | 9·104 | 73·439 | 64·707 |
| 3600 | 6·090 | 51·654 | 46·440 | 9·110 | 73·695 | 64·953 |
| 3700 | 6·168 | 51·822 | 46·583 | 9·115 | 73·945 | 65·192 |
| 3800 | 6·245 | 51·987 | 46·723 | 9·121 | 74·188 | 65·426 |
| 3900 | 6·320 | 52·150 | 46·860 | 9·126 | 74·425 | 65·654 |
| 4000 | 6·393 | 52·311 | 46·995 | 9·131 | 74·656 | 65·876 |
| 4100 | 6·464 | 52·470 | 47·126 | 9·136 | 74·882 | 66·093 |
| 4200 | 6·532 | 52·627 | 47·255 | 9·140 | 75·102 | 66·305 |
| 4300 | 6·597 | 52·781 | 47·382 | 9·145 | 75·317 | 66·512 |
| 4400 | 6·659 | 52·933 | 47·506 | 9·149 | 75·527 | 66·714 |
| 4500 | 6·717 | 53·084 | 47·629 | 9·153 | 75·733 | 66·912 |
| 4600 | 6·773 | 53·232 | 47·749 | 9·157 | 75·934 | 67·106 |
| 4700 | 6·825 | 53·378 | 47·867 | 9·160 | 76·131 | 67·296 |
| 4800 | 6·873 | 53·522 | 47·983 | 9·164 | 76·324 | 67·482 |
| 4900 | 6·918 | 53·665 | 48·098 | 9·166 | 76·513 | 67·665 |
| 5000 | 6·960 | 53·805 | 48·211 | 9·168 | 76·698 | 67·844 |

For tetratomic phosphorus vapour the values vary slightly from those given above and complete data are shown in Table XLII.

For the $P_4$ data (Table XLII) the information available was sufficient only to make a rigid rotator-harmonic oscillator approximation in the calculation of the internal partition function. The figure of 103·652 given in the original paper for the entropy at 2000°K. appears to be in error.

For data in Table XLII the $P_4$ frequencies used were 363, 461 and 606 cm.$^{-1}$, with a moment of inertia of $251{\cdot}17 \times 10^{-40}$ g. cm.$^2$ The spectroscopic data for the $P_2$ molecule are given in Table XLIII.

The heats of formation to be used with the functions given in Tables XLI and XLII are given in Table XLIV. These are referred to crystalline, white β-phosphorus

*Table XLII.—Thermodynamic Functions of* $P_4(g)$ *in the Ideal Gas State*
(All entropy data in g.-cal. mole$^{-1}$ deg.$^{-1}$)

| Temp. (°K.) | $C_p^\circ$ | $S^\circ$ | $-\left(\frac{G^\circ - H_0^\circ}{T}\right)$ | Temp. (°K.) | $C_p^\circ$ | $S^\circ$ | $-\left(\frac{G^\circ - H_0^\circ}{T}\right)$ |
|---|---|---|---|---|---|---|---|
| 273·15 | 15·539 | 65·541 | 54·602 | 2600 | 19·809 | 107·843 | 89·399 |
| 298·15 | 16·075 | 66·926 | 55·578 | 2700 | 19·813 | 108·591 | 90·096 |
| 300 | 16·111 | 67·025 | 55·648 | 2800 | 19·817 | 109·312 | 90·770 |
| 400 | 17·526 | 71·876 | 59·119 | 2900 | 19·821 | 110·007 | 91·421 |
| 500 | 18·293 | 75·877 | 62·083 | 3000 | 19·824 | 110·679 | 92·052 |
| 600 | 18·743 | 79·256 | 64·671 | 3100 | 19·827 | 111·329 | 92·664 |
| 700 | 19·028 | 82·167 | 66·967 | 3200 | 19·830 | 111·959 | 93·257 |
| 800 | 19·219 | 84·722 | 69·030 | 3300 | 19·833 | 112·569 | 93·833 |
| 900 | 19·353 | 86·993 | 70·902 | 3400 | 19·835 | 113·161 | 94·393 |
| 1000 | 19·448 | 89·038 | 72·615 | 3500 | 19·837 | 113·736 | 94·937 |
| 1100 | 19·521 | 90·895 | 74·194 | 3600 | 19·839 | 114·295 | 95·467 |
| 1200 | 19·576 | 92·596 | 75·657 | 3700 | 19·841 | 114·839 | 95·983 |
| 1300 | 19·619 | 94·164 | 77·021 | 3800 | 19·843 | 115·368 | 96·487 |
| 1400 | 19·654 | 95·620 | 78·299 | 3900 | 19·844 | 115·883 | 96·977 |
| 1500 | 19·681 | 96·977 | 79·499 | 4000 | 19·845 | 116·386 | 97·456 |
| 1600 | 19·704 | 98·248 | 80·632 | 4100 | 19·847 | 116·876 | 97·924 |
| 1700 | 19·723 | 99·443 | 81·703 | 4200 | 19·848 | 117·354 | 98·381 |
| 1800 | 19·739 | 100·571 | 82·720 | 4300 | 19·849 | 117·821 | 98·828 |
| 1900 | 19·753 | 101·638 | 83·688 | 4400 | 19·850 | 118·277 | 99·264 |
| 2000 | 19·765 | 102·652 | 84·611 | 4500 | 19·851 | 118·723 | 99·692 |
| 2100 | 19·775 | 103·616 | 85·493 | 4600 | 19·852 | 119·160 | 100·110 |
| 2200 | 19·783 | 104·536 | 86·338 | 4700 | 19·853 | 119·587 | 100·520 |
| 2300 | 19·791 | 105·416 | 87·149 | 4800 | 19·854 | 120·005 | 100·922 |
| 2400 | 19·797 | 106·258 | 87·928 | 4900 | 19·855 | 120·414 | 101·316 |
| 2500 | 19·803 | 107·067 | 88·677 | 5000 | 19·855 | 120·815 | 101·702 |

*Table XLIII.—Spectroscopic Data for the* $P_2$ *Molecule*

| Electronic state | $\nu_{00}$ (cm.$^{-1}$) | $\omega_e$ (cm.$^{-1}$) | $\omega_e X_e$ (cm.$^{-1}$) | $B_e$ (cm.$^{-1}$) | $\alpha_e$ (cm.$^{-1}$) | $D_e \times 10^6$ (cm.$^{-1}$) | $D_0$ (cm.$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $^1\Sigma_g^+$ | | 780·89 | 2·82 | 0·30359 | 0·001477 | 0·185 | 40598 |
| $^1\pi_g$ | 34434·3 | 618·88 | 2·97 | 0·2752 | 0·00169 | 0·20 | 40598 |

as the standard state. They are based on a heat of sublimation of α-white phosphorus of 14,040 g.-cal.[194] and the value of $H_{298}^\circ - H_0^\circ$ allowing for the α to β transition.

Slightly different values for the free energy of monatomic phosphorus gas have been reported[339] for temperatures up to 8000°K. These were calculated by the method

*Table XLIV.—Heats of Formation of Phosphorus referred to Crystalline, β-White Phosphorus at* 0°K.

| | $\Delta H_0^\circ$ (g.-cal. mole$^{-1}$) | $\Delta H_{298\cdot15}^\circ$ (g.-cal. mole$^{-1}$) |
|---|---|---|
| P | 75,370 | 75,580 |
| $P_2$ | 34,690 | 34,250 |
| $P_4$ | 15,760 | 14,040 |

of Giauque[340] using a constant of $-7{\cdot}28632$ g.-cal. mole$^{-1}$ deg.$^{-1}$ in the Sackur–Tetrode free energy equation. The gas constant used was $\boldsymbol{R} = 1{\cdot}98780$ g.-cal. mole$^{-1}$ deg.$^{-1}$ and for the ratio $hc/k$ the value was 1·43880 cm. deg. The data are given in Table XLV.

*Table XLV.—Free Energy of Monatomic Phosphorus Vapour*

| Temp. (°K.) | $-\left(\frac{G^\circ_T - H^\circ_0}{T}\right)$ g.-cal. (mole P)$^{-1}$ deg.$^{-1}$ |
|---|---|
| 298·16 | 34·020 |
| 500 | 36·590 |
| 1000 | 40·034 |
| 1500 | 42·049 |
| 2000 | 43·480 |
| 2500 | 44·595 |
| 3000 | 45·515 |
| 4000 | 47·008 |
| 5000 | 48·225 |
| 6000 | 49·268 |
| 7000 | 50·185 |
| 8000 | 51·002 |

The value of $H^\circ_{298\cdot16} - H^\circ_0$ was 1481·7 g.-cal./mole P.

It has been reported[341] that the assumption of a simple valency field force is not satisfactory for the calculation of the thermodynamic functions of the $P_4$ molecule (see also ref. 336, p. 299). An attempt was made to correct the anharmonicity in a semi-quantitative manner. The corrected values of $\omega_1 + 2x_{11} + x_{12} = 604$, $\omega_2 + \frac{1}{2}x_{12} = 381$ and $\omega_3 = 506$ were obtained[341] instead of the usual vibration frequencies of $\nu_1 = 606$ cm.$^{-1}$, $\nu_2 = 363$ cm.$^{-1}$ and $\nu_3 = 464\cdot5$ cm.$^{-1}$ The thermodynamic properties of $P_4$ gas have been calculated for ideal gas at 1 atmosphere pressure, by using these corrected frequencies and a rigid rotator-harmonic oscillator model.[342] However, this procedure has been criticized[343] and it would seem that it gives less accurate values of the thermodynamic functions than those obtained[171–2] directly from the uncorrected, observed vibrational wave numbers.

## Thermodynamics of Sublimation

There is some uncertainty in the earlier data[155] for the thermodynamics of sublimation of white phosphorus owing to various values which had been reported for the heat of sublimation of α-white phosphorus (see pages 165–166 and 192–193).

The thermodynamic constants at 298·16°K. for the sublimation of α-white phosphorus, based on a heat of sublimation of 13·47 kcal./mole $P_4$, have been given as[155]

$$\begin{aligned}\Delta H^\circ &= 13{,}470 \text{ g.-cal./mole } P_4\\ \Delta G^\circ &= 5784 \pm 8 \text{ g.-cal./mole } P_4\\ \Delta S^\circ &= 25\cdot78 \pm 0\cdot03 \text{ g.-cal./mole } P_4\text{/deg.}\end{aligned}$$

The corresponding thermodynamic equations are:

$$\begin{aligned}\Delta C^\circ_p &= 5\cdot515 - 28\cdot210 \times 10^{-3}T - 2\cdot98 \times 10^5 T^{-2}\\ \Delta H^\circ &= 12{,}080 + 5\cdot515T - 14\cdot105 \times 10^{-3}T^2 + 2\cdot98 \times 10^5 T^{-1}\\ \Delta G^\circ &= 12{,}080 + 4\cdot396T - 12\cdot699T \log_{10} T + 14\cdot105 \times 10^{-3}T^2 + 1\cdot49 \times 10^5 T^{-1}\\ \Delta S^\circ &= 1\cdot119 + 12\cdot699 \log_{10} T - 28\cdot21 \times 10^{-3}T + 1\cdot49 \times 10^5 T^{-2}\end{aligned}$$

These expressions are derived from the heat capacity equations for solid white phosphorus[192] and for $P_4$ vapour[191] (see page 194). The figure of 12,080 was calculated from the heats of fusion[192] and vaporization[182] of 601 and 12,750 g.-cal./mole $P_4$ respectively at the melting point, 44·1°C. The constant 5·515 is in error and should be 5·612.

More reliable equations may be derived by using the later and more accurate heat of sublimation of 14,040 g.-cal.(mole $P_4$)$^{-1}$ at 25°C.[194] Entropy values at 25°C. of 39·2 g.cal.(mole $P_4$)$^{-1}$ deg.$^{-1}$ for solid α-white phosphorus[172, 335] and 66·93 g.-cal.(mole $P_4$)$^{-1}$ deg.$^{-1}$ for $P_4$ vapour[335] give an entropy of sublimation of 27·73 g.-cal.(mole $P_4$)$^{-1}$ deg.$^{-1}$, and the following equations:

$$\begin{aligned}
\Delta C_p^\circ &= 5{\cdot}612 - 28{\cdot}210 \times 10^{-3}T - 2{\cdot}975 \times 10^{5}T^{-2} \\
\Delta H^\circ &= 12{,}623 + 5{\cdot}612T - 14{\cdot}105 \times 10^{-3}T^{2} + 2{\cdot}975 \times 10^{5}T^{-1} \\
\Delta G^\circ &= 12{,}623 - 12{\cdot}922 \log_{10} T + 3{\cdot}123T + 14{\cdot}105 \times 10^{-3}T^{2} + 1{\cdot}488 \times 10^{5}T^{-1} \\
\Delta S^\circ &= 2{\cdot}489 + 12{\cdot}922 \log_{10} T - 28{\cdot}21 \times 10^{-3}T + 1{\cdot}488 \times 10^{5}T^{-2}
\end{aligned}$$

The thermodynamic constants at 25°C. are:

$$\begin{aligned}
\Delta H^\circ &= 14{,}040 \text{ g.-cal.(mole } P_4)^{-1} \\
\Delta G^\circ &= 5{,}773 \text{ g.-cal.(mole } P_4)^{-1} \\
\Delta S^\circ &= 27{\cdot}73 \text{ g.-cal.(mole } P_4)^{-1} \text{ deg.}^{-1}
\end{aligned}$$

The sublimation pressure at 25°C. as measured by Centnerszwer[190] gives a free energy value of 5,792 g.-cal.(mole $P_4$)$^{-1}$.[154]

### Thermodynamics of Dissociation

The experimental data[201] for the dissociation $P_4 \rightleftharpoons 2P_2$ fit the following equation for the dissociation constant in the temperature range 900° to 1200°C.

$$\log_{10} K_{\text{atm.}} = 7{\cdot}5787 - 11{\cdot}489T^{-1}$$

(see page 168 and ref. 155, p. 16).

This gives an average heat of dissociation $\Delta H^\circ = 52{,}550$ g.-cal. The expression for the free energy of dissociation is

$$\Delta G^\circ = 52{,}550 - 34{\cdot}665T$$

Calculations based on spectroscopic data[77] give the following equations:

$$\begin{aligned}
\log_{10} K_{\text{atm.}} &= 7{\cdot}582 - 11{,}505T^{-1} \\
\Delta G^\circ &= 52{,}650 - 34{\cdot}690T
\end{aligned}$$

The heat of dissociation at 0°K. was calculated[77] to be $\Delta H_0^\circ = 53{,}600$ g.-cal. Using this value and the thermodynamic properties of $P_4$ and $P_2$ given in Table XLII and Table XXXIX, the data in Table XLVI are obtained.

*Table XLVI.—Thermodynamics of the Dissociation* $P_4 \rightleftharpoons 2P_2$

| Temp. (°K.) | $\Delta G^\circ$ (g.-cal. mole$^{-1}$) | $\Delta H^\circ$ (g.-cal. mole$^{-1}$) | $\Delta S^\circ$ (g.-cal. mole$^{-1}$ deg.$^{-1}$) | $K_p$ (atm.) | % dissociation |
|---|---|---|---|---|---|
| 298·1 | 43,375 | 54,498 | 37·29 | $1{\cdot}6 \times 10^{-32}$ | $6 \times 10^{-15}$ |
| 1000 | 17,942 | 53,303 | 35·36 | $1{\cdot}18 \times 10^{-4}$ | 0·54 |
| 1173 | 12,000 | 53,240 | 35·16 | $5{\cdot}84 \times 10^{-3}$ | 3·8 |
| 1200 | 10,880 | 52,935 | 35·06 | $1{\cdot}05 \times 10^{-2}$ | 5·1 |
| 1273 | 8,360 | 52,810 | 34·92 | $3{\cdot}66 \times 10^{-2}$ | 9·5 |
| 1300 | 7,380 | 52,750 | 34·90 | $5{\cdot}76 \times 10^{-2}$ | 12·1 |
| 1373 | 4,880 | 52,630 | 34·78 | 0·167 | 20·0 |
| 1400 | 3,910 | 52,570 | 34·76 | 0·245 | 24·1 |
| 1473 | 1,380 | 52,440 | 34·66 | 0·624 | 36·7 |
| 1500 | 425 | 52,390 | 34·64 | 0·867 | 42·1 |
| 1600 | −3,006 | 52,210 | 34·51 | 2·58 | 62·6 |
| 1800 | −9,900 | 51,860 | 34·31 | 15·95 | 89·4 |
| 2000 | −16,720 | 51,500 | 34·11 | 91·75 | 97·9 |

Similar calculations for the $P_2 \rightleftharpoons 2P$ dissociation, using a heat of dissociation of 116,000 g.-cal. mole$^{-1}$ (5·031 e.v.)[171–2] at 0°K. give the results shown in Table XLVII.

The thermodynamic properties used for the above calculation were taken from Table XXXIX and Table XLI.

*Table XLVII.—Thermodynamics of the Dissociation* $P_2 \rightleftharpoons 2P$

| Temp. (°K.) | $\Delta G°$ (g.-cal. mole$^{-1}$) | $\Delta H°$ (g.-cal. mole$^{-1}$) | $\Delta S°$ (g.-cal. mole$^{-1}$ deg.$^{-1}$) | $K_p$ (atm.) | % dissociation |
|---|---|---|---|---|---|
| 298·1 | 109,125 | 116,830 | 25·85 | $1·1 \times 10^{-80}$ | $5 \times 10^{-39}$ |
| 1000 | 90,090 | 117,870 | 27·78 | $2 \times 10^{-20}$ | $7 \times 10^{-9}$ |
| 1500 | 76,090 | 118,400 | 28·21 | $8·2 \times 10^{-12}$ | $4·5 \times 10^{-4}$ |
| 2000 | 61,890 | 118,927 | 28·52 | $1·7 \times 10^{-7}$ | $1 \times 10^{-2}$ |
| 2500 | 47,570 | 119,570 | 28·80 | $6·9 \times 10^{-5}$ | 0·42 |
| 3000 | 33,080 | 120,473 | 29·13 | $3·9 \times 10^{-3}$ | 3·13 |
| 3500 | 18,420 | 121,760 | 29·53 | $7·1 \times 10^{-2}$ | 13·2 |
| 4000 | 3,560 | 123,410 | 29·97 | 0·64 | 37·2 |
| 4500 | −11,560 | 125,400 | 30·44 | 3·64 | 69·1 |
| 5000 | −26,890 | 127,660 | 30·91 | 14·9 | 88·8 |

The data of Table XLVII fit the following equation for the equilibrium constant:

$$\log_{10} K_{\text{atm.}} = 6·426 - 26{,}230T^{-1}$$

which gives an average heat of dissociation of $\Delta H° = 120{,}200$ g.-cal.(mole $P_2$)$^{-1}$.

The corresponding free energy equation is

$$\Delta G° = 120{,}200 - 29·4T$$

The dissociation of the tetratomic and diatomic vapour is shown graphically in Fig. 15.

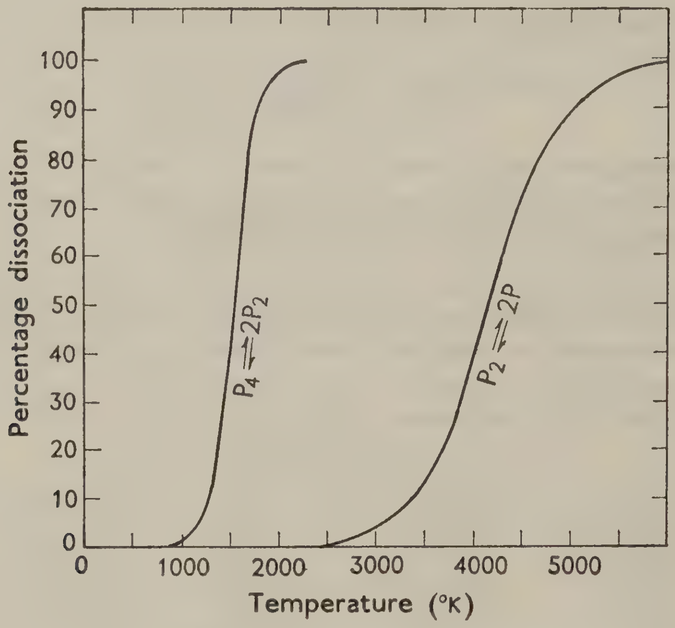


FIG. 15.—Dissociation of phosphorus vapour

## Thermodynamic Properties of Liquid Phosphorus

The vapour pressure of liquid phosphorus between 44° and 360°C. is represented by the equation[155]

$$\log_{10} p_{\text{mm.}} = 18·8192 + 1·074 \times 10^{-3}T - 3·906 \log_{10}T - 3216·7T^{-1}$$

From this, by means of the relation

$$\frac{d(\log_e p)}{dT} = \frac{\Delta H}{RT^2}$$

the latent heat of vaporization is given by

$$\Delta H^\circ = 14{,}714-7{\cdot}7603T+4{\cdot}9122\times10^{-3}T^2 \text{ g.-cal.(mole } P_4)^{-1}$$

The corresponding free energy and entropy equations are:

$$\Delta G^\circ = 14{,}714-72{\cdot}918T-4{\cdot}912\times10^{-3}T^2+17{\cdot}872T\log_{10}T$$
$$\Delta S^\circ = 65{\cdot}158+9{\cdot}826\times10^{-3}T-17{\cdot}872\log_{10}T$$

The heat capacity equation for liquid phosphorus in the temperature range 25°C. to 97°C. is[192]

$$C_p^\circ = 24{\cdot}151+11{\cdot}932\times10^{-3}T-3{\cdot}927\times10^{-5}T^2 \text{ g.-cal.(mole } P_4)^{-1}\text{ deg.}^{-1}$$

A summary of the data derived from these equations is given in Table XLVIII.

*Table XLVIII.—Thermodynamic Properties of Liquid Phosphorus*[155]

| Temp. (°K.) | Vapour pressure (atm.) | Free energy of vaporization (g.-cal./mole) |  | Heat of vaporization ($\Delta H^\circ$) | Entropy |  |  | $C_p^\circ$ (liquid) |
|---|---|---|---|---|---|---|---|---|
|  |  | ($\Delta G^\circ$) | ($\Delta G_c^\circ$) |  | Vaporization | $P_4$ (g) | $P_4$ (liquid) |  |
| 317·26 | 0·000233 | 5270 | 5270 | 12,750 | 23·6 | 67·9 | 44·3 | 23·98 |
| 373·1 | 0·00469 | 3970 | 3960 | 12,500 | 22·9 | 70·6 | 47·7 | 23·14 |
| 423·1 | 0·03395 | 2840 | 2840 | 12,310 | 22·4 | 72·8 | 50·4 | 22·2 |
| 473·1 | 0·158 | 1730 | 1740 | 12,140 | 22·0 | 74·8 | 52·8 | 21·0 |
| 523·1 | 0·538 | 640 | 660 | 12,000 | 21·7 | 76·6 | 54·9 | 19·6 |
| 553·7 | 1·0 | 0 | 0 | 11,920 | 21·5 | 77·7 | 56·2 | 18·7 |
| 573·1 | 1·467 | −440 | −420 | 11,880 | 21·5 | 78·3 | 56·8 | 18·1 |
| 623·1 | 3·378 | −1510 | −1500 | 11,790 | 21·3 | 79·9 | 58·6 | 16·3 |

The entropy values for $P_4(g)$ used in the above Table were derived from the free energy and heat content data of Stevenson and Yost.[77]

The free energy of vaporization has also been obtained[155] from the heat capacity equation for liquid phosphorus given above, and the heat capacity equation for phosphorus vapour,[191] i.e.,

$$C_p^\circ\text{ (gas)} = 19{\cdot}23+0{\cdot}510\times10^{-3}T-2{\cdot}980\times10^{5}T^{-2} \text{ g.-cal.(mole } P_4)^{-1}\text{ deg.}^{-1}$$

This gives the following free energy equation

$$\Delta G_c^\circ = 13{,}638+11{\cdot}331T\log_{10}T-57{\cdot}358T+5{\cdot}711\times10^{-3}T^2 \\ -0{\cdot}6545\times10^{-5}T^3+1{\cdot}490\times10^{5}T^{-1}$$

the values of which are given in column 4 of Table XLVIII. The agreement between the two sets of free energy data has been taken as evidence that the heat capacity equation for liquid phosphorus is reliable up to 350°C.[155] On the other hand the following heat content and entropy equations may be derived from the heat capacity equations:

$$\Delta H^\circ = 13{,}638-4{\cdot}92T-5{\cdot}71\times10^{-3}T^2+2{\cdot}98\times10^{5}T^{-1}+1{\cdot}31\times10^{-5}T^3$$
$$\Delta S^\circ = 52{\cdot}44-11{\cdot}33\log_{10}T-11{\cdot}42\times10^{-3}T+1{\cdot}49\times10^{5}T^{-2}+1{\cdot}964\times10^{-5}T^2$$

These expressions have the property of giving minimum values for the heat content and entropy at about 600°K.

The vapour pressure equation of supercooled red phosphorus is[182]

$$\log_{10}p_{\text{atm.}} = 8{\cdot}6886-2898{\cdot}1T^{-1}-1{\cdot}2566\log_{10}T$$

The following thermodynamic expressions may be derived from this equation:

$$\begin{aligned}
\Delta G^\circ &= 13{,}256 - 39{\cdot}74T + 5{\cdot}748T \log_{10} T \\
\Delta H^\circ &= 13{,}256 - 2{\cdot}893T \\
\Delta S^\circ &= 36{\cdot}85 - 5{\cdot}748 \log_{10} T
\end{aligned}$$

These give the data shown in Table XLIX.

*Table XLIX.—Thermodynamic Properties of Supercooled Red Phosphorus*

| Temp. (°K.) | Vapour pressure (atm.) | Free energy of vaporization ($\Delta G^\circ$) (g.-cal./mole) | Heat of vaporization ($\Delta H^\circ$) (g.cal./mole) | Entropy | | |
|---|---|---|---|---|---|---|
| | | | | Vaporization | $P_4$ (g) | $P_4$ (liquid) ($\Delta S^\circ$) |
| 400 | 0·0149 | 3343 | 12,100 | 21·89 | 71·86 | 49·97 |
| 500 | 0·317 | 1143 | 11,810 | 21·34 | 75·84 | 54·50 |
| 600 | 2·374 | −1006 | 11,520 | 20·88 | 79·24 | 58·36 |
| 700 | 9·367 | −3013 | 11,240 | 20·49 | 82·13 | 61·64 |
| 800 | 26·16 | −5186 | 10,940 | 20·16 | 84·67 | 64·51 |
| 900 | 57·10 | −7227 | 10,650 | 19·87 | 86·94 | 67·07 |
| 1000 | 104·8 | −9243 | 10,360 | 19·61 | 89·05 | 69·44 |

## Bond Energies and Related Properties

Since 1950 many thermochemical investigations which provide information on phosphorus bonds and bond energies have been made on phosphorus compounds. Most of the thermochemical data are derived from reaction calorimetry. Combustion measurements, especially with high-precision calorimeters, are relatively rare. Because of this, the accuracy in phosphorus thermochemistry is lower than that for other elements such as carbon. In addition, revisions or more accurate measurements of some of the earlier data necessitate alterations in the values of some of the thermochemical properties of phosphorus. Critical reviews[117, 344] of the subject have given assessments of the accuracy and reliability of the information at present available.

The term 'bond energy' is sometimes used without precise definition, so that confusion arises over its meaning and interpretation. In the present account the concept is used to indicate the strength of a bond in two ways.[302] The bond strength may be measured by determining how much energy is required to break the bond. This value is referred to as the bond dissociation energy, $D_0^\circ$. The latter is defined[345] as the change in energy, $\Delta E_0^\circ$ at absolute zero in the ideal gas state, required to break the bond $X$–$Y$ according to the reaction

$$XY \rightarrow X + Y$$

with the products in their ground state. In polyatomic molecules the bond dissociation energy may include energy associated with changes in the spatial arrangement of the remaining atoms or adjustment of the other bonds in the molecule, consequent upon the breaking of a particular bond.

The alternative is to use a quantity which, when summed over all the bonds, gives the heat of formation of a molecule from atoms. This quantity is referred to as the thermochemical bond energy term $E$. Unlike the bond dissociation energy, the thermochemical bond energy term is referred to 298·16°K. and not to 0°K. This is because data are not always available to enable the zero-point energy to be calculated (see ref. 302, pp. 103–6). The bond energy term is therefore defined as the quantity obtained by summation over all bonds and is the heat of atomization in the ideal gas state at 298·16°K. to the atomic elements in their ground state at this temperature.[123, 302] It should be noted that this definition refers only to the gaseous state. If, therefore, the heat of atomization is given for a solid or liquid, the latent heat of fusion and vaporization must be subtracted in order to allow for the Van der Waals forces which take no part in bond formation. For a gaseous compound the heat of atomization is obtained by adding to its heat of formation, $-\Delta H_1$ (in the ideal gas state from its elements in their standard state), the sum of the heats of formation, $\Sigma\Delta H_2$ (from the elements in their standard states), of the monatomic gaseous elements.

In a diatomic molecule the bond energy term is equal to the bond dissociation energy, but for polyatomic molecules the bond energy terms are not usually equal to one another. For example the bond dissociation energy for P–O in phosphorus monoxide is 140 kcal. mole$^{-1}$ but in phosphorous oxide ($P_4O_6$) the bond energy term $E$(P–O) is 86 kcal. mole$^{-1}$.

The literature contains some bond energy values which have since been revised in the light of more reliable data. For example, the P–P bond energy term has been reported[123] to be 18·9 kcal. mole$^{-1}$. This was based on an early value of 42 kcal. mole$^{-1}$ for the heat of dissociation of diatomic phosphorus vapour. Correction for the more accurate value of 116 kcal. mole$^{-1}$ gives[108] a bond energy of 48 kcal. mole$^{-1}$. The bond energy data given below have been selected from what is considered to be the most reliable information.

The bond-dissociation energies of the diatomic molecules PC,[302, 346] PP,[76, 302, 346] PN[344, 347] and PO,[302, 344, 348] in kcal. mole$^{-1}$ are $138 \pm 23$, $117 \pm 1$, $164 \pm 2$ and $140 \pm 20$, respectively. The value for PN replaces those previously given.[76, 302, 346]

For polyatomic molecules, difficulties arise in assigning values to the various bonds involved. For simple compounds resulting from the combination of only two kinds of atoms, e.g., $PH_3$, $PCl_3$, an average value $\bar{E}$ of the bond energy terms can be obtained from heats of formation as described above. The figure obtained in this way is based on the assumption that the same energy is required to break each bond in succession. This assumption may not be valid where the molecular configuration alters with the breaking of the initial bond. Table L gives average bond energy terms for a number of phosphorus bonds.[344]

*Table L.—Average Bond Energy Terms in Phosphorus Compounds*

| Compound | Bond | $\bar{E}$ (kcal. mole$^{-1}$) | Compound | Bond | $\bar{E}$ (kcal. mole$^{-1}$) |
|---|---|---|---|---|---|
| $PH_3$ | P–H | 77 | $PI_3$ | P–I | 44 |
| $PF_3$ | P–F | 117 | $P_4O_6$ | P–O | 86 |
| $PCl_3$ | P–Cl | 76 | $P_4$ | P–P | 48 |
| $PBr_3$ | P–Br | 62 | | | |

Some of the above values differ slightly from those reported elsewhere[302] through the use of more accurate data, which are summarized in Table LII. A few of the data for phosphorus halides are either incomplete or depend on very early investigations. In particular, the heat of sublimation of phosphorus tri-iodide is an estimate. The bond energy term for P–O is based on a recent determination of the heat of formation of phosphorous oxide[304] which is considered to be more reliable than the earlier value.[300] The value of $\bar{E}$(P–P) refers to the $P_4$ tetrahedron with a bond angle of 60°. Several attempts have been made to correct this for the so-called strain energy. The normal angle between the *p*-orbitals in the phosphorus tetrahedron is 90°. By assuming an overlap of wave functions, the angle of strain is 15°, i.e., $\frac{1}{2}(90° - 60°)$. The bond energy for a normal or unstrained bond is therefore $\bar{E}\sec.^2 15$ or 51·5 kcal. This gives a strain energy of 3·5 kcal. per P–P bond or 21 kcal.(mole $P_4$)$^{-1}$.[108] The observed bond angle for phosphorus is, however, very nearly 101° and from this a strain energy of 22·8 kcal. (mole $P_4$)$^{-1}$ has been calculated,[64] thus making $\bar{E} = 51{\cdot}8$ kcal. The strain energy has also been calculated to be 42 kcal.(mole $P_4$)$^{-1}$, i.e $\bar{E} = 55$ kcal.[109]

An estimated value of 53 kcal has been obtained for an unstrained P–P bond.[124]

This is based on the heat of sublimation of red phosphorus to diatomic vapour and is therefore not comparable with the values discussed above. It assumes that the $P_2$ molecule is triple-bonded. A thermochemical bond energy $\bar{E} = 46{\cdot}8$ kcal. has been obtained from the heat of formation (+5 kcal. mole$^{-1}$) of $P_2H_4$ and the P–H bond energy given in Table L.[349]

*Table LI.—Heats of Atomization of Elements at* 298°K.[302]

| Element | Standard state | $\Delta H_{\text{at.}}$ (kcal. per g. atom) | Element | Standard state | $\Delta H_{\text{at.}}$ (kcal. per g. atom) |
|---|---|---|---|---|---|
| Hydrogen | $H_2(g)$ | 52·09 | Chlorine | $Cl_2(g)$ | 28·94 |
| Carbon | graphite($c$) | 170·9 | Bromine | $Br_2(l)$ | 26·71 |
| Nitrogen | $N_2(g)$ | 112·9 | Iodine | $I_2(c)$ | 25·48 |
| Oxygen | $O_2(g)$ | 59·54 | Phosphorus | $P(c)$ | 75·5 |
| Fluorine | $F_2(g)$ | 18·5 | Sulphur | $S(c)$ | 57 |

Of the above values, that for sulphur is the only doubtful one.

*Table LII.—Thermochemical Data for Phosphorus Compounds*[344]

| Compound | $\Delta H^\circ_{298}$ (kcal. mole$^{-1}$) | | | Ref. |
|---|---|---|---|---|
| | Vaporization | Sublimation | Formation (gas) | |
| $PF_3$ | — | — | −221·0 | 350 |
| $PCl_3$ | 7·8 | — | −65·5 | 351, 352 |
| $PBr_3$ | 11·6 | — | −28·9 | 353 |
| $PI_3$ | — | — | −10·5, −10·9(a) | 354, 355 |
| $P_2I_4$ | — | 30(b) | +10·0 | 299, 356 |
| $PCl_5$ | — | 15·35 | −95·35 | 299 |
| $PBr_5$ | — | 13·0 | −53·0 | 299 |
| $PH_3$ | — | — | +1·3 | 349 |
| $P_2H_4$ | — | — | +5·0 | 349 |
| $POF_3$ | — | — | −292 | 356 |
| $POCl_3$ | 9·22 | 12·4 | −134·0 | 352, 357, 358 |
| $POBr_3$ | — | 15·0 | −94·0 | 352 |
| $PO(NCO)_3$ | 13·4(b) | — | −158·6 | 359–61 |
| $(PNCl_2)_3$ | — | 18·2 | −175·9 | 362 |
| $(PNCl_2)_4$ | — | 23·1 | −236·1 | 362 |
| $C_2H_5POCl_2$ | 10·2 | — | −137·1 | 363 |
| $CH_3POCl_2$ | — | 14·9 | −133·9 | 363 |
| $[(CH_3)_2PN]_3$ | — | — | −125·1(a) | 364 |
| $[(C_6H_5)_2PN]_4$ | — | — | +40·7(a) | 364 |
| $[(cyclo\text{-}C_6H_{11}O)_2PN]_3$ | — | — | −582·0(a) | 364 |
| $(CH_3)_3P$ | 6·92 | — | −23·2 | 365 |
| $(C_6H_5)_3P$ | — | 18·1(b) | +72·4 | 366 |
| $(CH_3)_3PO$ | — | 12·0 | −103·0 | 367 |
| $(C_6H_5)_3PO$ | — | 19·1(b) | +3·5 | 366 |
| $[(CH_3)_3N]_3PO$ | 13·5 | — | −114·1 | 368, 369 |
| $(CH_3)_3PNC_2H_5$ | 12·0 | — | −24·6 | 367 |
| $(C_6H_5)_3PNC_2H_5$ | 13·0 | — | +40 | 367 |
| $(C_6H_5NH)_2CH_3PO$ | — | — | −86·6(a) | 363 |
| $(C_6H_5NH)_2C_2H_5PO$ | — | — | −89·6(a) | 363 |
| $[(CH_3)_2N]_3P$ | 13(b) | — | −32·0 | 369 |
| $[(C_2H_5)_2N]_3P$ | 14·5 | — | −52·3 | 368 |
| $(CH_3O)_3P$ | 9·0(b) | — | −166 | 370 |
| $(C_2H_5O)_3P$ | 10·0 | — | −193·5 | 363 |
| $(iso\text{-}C_3H_7O)_3P$ | 11·0 | — | −224 | 363 |
| $(C_2H_5O)_3PO$ | 12·2 | — | −285·6 | 366, 368, 371 |
| $(iso\text{-}C_3H_7O)_3PO$ | 13·0(b) | — | −310·9 | 368, 369 |

Notes: (a) $\Delta H^\circ_f$ for solid; (b) Estimated.

The heats of atomization used in deriving $\bar{E}$ values for some gaseous atoms are given in Table LI.

Thermochemical data for a number of phosphorus compounds are summarized in Table LII, at a temperature of 298°K.

Average values of the thermochemical bond energies ($\bar{E}$) have been calculated[344] for some tervalent organic phosphorus compounds. These were evaluated by deducting from the heat of formation of the compound the heat of formation of the organic group. The values so obtained are given in Table LIII.

*Table LIII.—Average Bond Energy Terms for Organo-phosphorus Compounds*[344]

| Compound | Bond | $\bar{E}$ (kcal. mole$^{-1}$) |
|---|---|---|
| $(CH_3O)_3P$ | P–O | 91 |
| $(C_2H_5O)_3P$ | P–O | 92 |
| $(iso\text{-}C_3H_7O)_3P$ | P–O | 92 |
| $(CH_3)_3P$ | P–C | 65 |
| $(C_6H_5)_3P$ | P–C | 71 |
| $[(CH_3)_2N]_3P$ | P–N | 70 |
| $[(C_2H_5)_2N]_3P$ | P–N | 67 |

Using the data given in Table LII the bond dissociation energy for the phosphoryl group P=O in a number of compounds has been evaluated.[344] This was done by considering heats of formation of compounds differing in composition by a single oxygen atom, or by using heats of reaction where direct oxidation reactions had been studied. The results are shown in Table LIV.

*Table LIV.—Average Bond Dissociation Energy of* P=O *in Phosphorus Compounds*[344]

| Compound | $D$(P=O) (kcal. mole$^{-1}$) |
|---|---|
| $P_4O_{10}$ | 138 |
| $POF_3$ | 130 |
| $POCl_3$ | 128 |
| $POBr_3$ | 125 |
| $PO(CH_3)_3$ | 139 |
| $PO(n\text{-}C_3H_7)_3$ | 138 |
| $PO(n\text{-}C_4H_9)_3$ | 137 |
| $PO(C_6H_5)_3$ | 128 |
| $PO(C_2H_5O)_3$ | 151 |
| $PO(iso\text{-}C_3H_7O)_3$ | 146 |
| $PO[(CH_3)_2N]_3$ | 139 |
| $PO(C_2H_5)_2N)_3$ | 156 |

A method of assigning bond energies in which allowance is made for changes in the environment of the bonds has been suggested.[344] On the basis that each P=O link involves one $\pi$ bond and each P–O link involves $\frac{1}{3}\pi$ bond, values of the average *in situ* bond energy $\bar{\epsilon}$(P=O) have been computed. These are summarized in Table LV.

Other procedures for calculating bond energies have been suggested,[372, 373] but these do not provide close agreement with known data. It has been reported that the bond moment, $\mu$, of a molecule can be expressed by the equation

$$\mu = C^2 er$$

where $e$ is the electronic charge, $r$ is the bond distance and

$$\frac{1}{C^2} = 1 - \left(\frac{H_t - E}{H_c - E}\right)$$

*Table LV.*—In situ *Bond Energies of Phosphorus Compounds*[344]

| Compound | *In situ* bond energy (kcal. mole$^{-1}$) | | | |
|---|---|---|---|---|
| | $\bar{\epsilon}$(P=O) | $\bar{\epsilon}$(P–O) | $\bar{\epsilon}$(P–Halogen) | $\bar{\epsilon}$(P–N) |
| $P_4O_{10}$ | 112 | 94·7 | — | — |
| $P_4O_6$ | — | 94·7 | — | — |
| $POF_3$ | 112 | — | 123 | — |
| $POCl_3$ | 108·5 | — | 82·5 | — |
| $POBr_3$ | 107 | — | 68 | — |
| $(PNCl_2)_3$ | — | — | 82·5 | 70 |
| $(PNCl_2)_4$ | — | — | 82·5 | 70 |
| $[PN(C_6H_5)_2]_4$ | — | — | — | 74 |
| $[PN(CH_3)_2]_3$ | — | — | — | 68 |
| $PO[N(CH_3)_2]_3$ | 105 | — | — | 81 |
| $PO[N(C_2H_5)_2]_3$ | 105 | — | — | 84 |
| $PO(OC_2H_5)_3$ | 107·5 | 106·5 | — | — |
| PO(O-*iso*-$C_3H_7)_3$ | 107 | 105 | — | — |

where $E$ is the bond energy and $H_i$ and $H_c$ are the energies of the ideal ionic and ideal covalent bonds respectively.[374] Calculated values agree with those observed for P–Cl, but not for P–Br and P–I bonds.

The force constants $k_1$, $k_2$ and $k_3$ for the tetrahedral $P_4$ molecule have been calculated to be 2·08, −0·12 and 0·08 × 10$^5$ dynes cm.$^{-1}$, respectively.[375] These are based on the vibration frequencies $\nu_1 = 606$, $\nu_2 = 363$ and $\nu_3 = 468$ cm.$^{-1}$ corresponding to the relation

$$\nu_1{}^2 + 8\nu_2{}^2 = 6\nu_3{}^2$$

The value of $k_2$ is negative, in agreement with the idea of a restoring force for angular deformation.

## Bond Refraction

Data on the bond-refraction properties of phosphorus, based on experimentally determined molecular refractions of several trialkyl phosphites and phosphates, have been reported.[376] The bond refraction for the P=O group was found by subtracting the molecular refraction of a phosphite from that of the corresponding phosphate. The value for P–O bonds was derived from refraction data for the phosphites by subtracting the refraction due to other bonds in the molecule and dividing by three. For this purpose the following bond values were used:

C–H = 1·676, C–C = 1·296, C–O = 1·460

The average values of the bond refraction, $R_D$, obtained in this way are 3·18 for the P–O bond and −1·23 for the P=O bond, both referred to sodium *D* lines at 20°C. The bond refraction for P–C is 3·71 based on data for alkyl phosphines. The information for the individual molecules is summarized in Table LVI.

The bond refractions of these phosphorus bonds are considered[376] to be evidence supporting the formulation of the phosphoryl linkage, P=O, as a co-ordinate bond P → O.

There are numerous data on the density and refractive index of organic phosphorus compounds in the recent literature.[378, 381–92] This information may be used to calculate molar refractivities $R_D$ for the sodium *D*-line, according to the expression

$$R_D = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$$

where $n$ is the refractive index, $M$ the molecular weight and $d$ is the density. The $R_D$ values can then be used to estimate the bond refraction for various phosphorus

*Table LVI.—Bond Refractions in Phosphorus Compounds*

| Compound | Density $d_4^{20}$ | Refractive index $n_D^{20}$ | Molar refraction | Bond refraction | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | P–O | P–C | P═O | P–Cl | |
| $(C_2H_5)_3P$ | 0·8001[(a)] | 1·4580[(a)] | 40·23 | — | 3·73 | — | — | 377 |
| $(n\text{-}C_3H_7)_3P$ | 0·8073[(b)] | 1·4560[(b)] | 53·96 | — | 3·66 | — | — | 377 |
| $(n\text{-}C_4H_9)_3P$ | 0·8120[(b)] | 1·4570[(b)] | 67·72 | — | 3·63 | — | — | 377 |
| $(n\text{-}C_5H_{11})_3P$ | 0·8206[(b)] | 1·4606[(b)] | 82·32 | — | 3·82 | — | — | 377 |
| $(CH_3O)_3P$ | 1·0472 | 1·4089 | 29·03 | 3·19 | — | — | — | 377 |
| $(C_2H_5O)_3P$ | 0·9663 | 1·4126 | 42·84 | 3·15 | — | — | — | 376, 377 |
| $(n\text{-}C_3H_7O)_3P$ | 0·9417 | 1·4282 | 56·94 | 3·19 | — | — | — | 376, 377 |
| $(iso\text{-}C_3H_7O)_3P$ | 0·9063 | 1·4110 | 57·07 | 3·23 | — | — | — | 376, 377 |
| $(n\text{-}C_4H_9O)_3P$ | 0·9174 | 1·4320 | 70·76 | 3·16 | — | — | — | 376, 377 |
| $(n\text{-}C_5H_{11}O)_3P$ | 0·9023[(b)] | 1·4353[(b)] | 84·56 | 3·13 | — | — | — | 376, 378 |
| $(CH_3O)_3PO$ | 1·2144 | 1·3963 | 27·74 | — | — | −1·29 | — | 376 |
| $(C_2H_5O)_3PO$ | 1·0695 | 1·4053 | 41·77 | — | — | −1·07 | — | 376 |
| $(n\text{-}C_3H_7O)_3PO$ | 1·0121 | 1·4165 | 55·66 | — | — | −1·28 | — | 376 |
| $(iso\text{-}C_3H_7O)_3PO$ | 0·9867 | 1·4057 | 55·79 | — | — | −1·28 | — | 376 |
| $(n\text{-}C_4H_9O)_3PO$ | 0·9766 | 1·4250 | 69·73 | — | — | −1·19 | — | 376 |
| $(n\text{-}C_5H_{11}O)_3PO$ | 0·9608 | 1·4319 | 83·26 | — | — | −1·30 | — | 379 |
| $CH_3OPCl_2$ | 1·3980 | 1·4773 | 26·92 | — | — | — | 8·82 | 377 |
| $C_2H_5OPCl_2$ | 1·2857 | 1·4718 | 32·00 | — | — | — | 8·84 | 377 |
| $n\text{-}C_3H_7OPCl_2$ | 1·2278 | 1·4641 | 36·22 | — | — | — | 8·63 | 377 |
| $n\text{-}C_4H_9OPCl_2$ | 1·1657 | 1·4608 | 41·20 | — | — | — | 8·80 | 377 |
| $PCl_3$ | 1·5761 | 1·5147 | 26·28 | — | — | — | 8·76 | 380 |
| $POCl_3$ | 1·6795 | 1·4609 | 25·06 | — | — | −1·22 | 8·76 | 380 |

Notes: (a) At 18°C.; (b) At 25°C.

*Table LVII.—Bond Refraction Values for* $P{=}S$ *in Organic Phosphorus Compounds*

| Compound | Relative density | Re-fractive index | $R_D$ | Compound | Relative density | Re-fractive index | $R_D$ | $R_D$ for $P{=}S$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| $(C_2H_5O)_3P$ | 0·9663 | 1·4126 | 42·84 | $(C_2H_5O)_3PS$ | 1·0756 | 1·4488 | 49·3 | 6·5 | 377, 393–5 |
| $(n\text{-}C_3H_7O)_3P$ | 0·9417 | 1·4282 | 56·94 | $(n\text{-}C_3H_7O)_3PS$ | 1·0177 | 1·4502 | 63·4 | 6·5 | 377, 381 |
| $(n\text{-}C_4H_9O)_3P$ | 0·9174 | 1·4320 | 70·76 | $(n\text{-}C_4H_9O)_3PS$ | 0·9871 | 1·4515 | 76·9 | 6·1 | 377, 381 |
| $(n\text{-}C_6H_{13}O)_3P$ | 0·8993 | 1·4417 | 98·2 | $(n\text{-}C_6H_{13}O)_3PS$ | 0·9492 | 1·4560 | 104·8 | 6·6 | 381 |
| $(n\text{-}C_8H_{17}O)_3P$ | 0·8922 | 1·4482 | 125·5 | $(n\text{-}C_8H_{17}O)_3PS$ | 0·9293 | 1·4592 | 132·4 | 6·9 | 381 |
| $(C_2H_5O)(CH_3O)_2P$ | 1·0259 | 1·4110 | 33·3 | $(C_2H_5O)(CH_3O)_2PS$ | 1·1631 | 1·4530 | 39·6 | 6·3 | 386–92 |
| $(C_2H_5O)(n\text{-}C_3H_7O)_2P$ | 0·9550 | 1·4215 | 51·5 | $(C_2H_5O)(n\text{-}C_3H_7O)_2PS$ | 1·0388 | 1·4475 | 58·2 | 6·7 | 386–92 |
| $(C_2H_5O)(\mathit{iso}\text{-}C_3H_7O)_2P$ | 0·9300 | 1·4150 | 52·1 | $(C_2H_5O)(\mathit{iso}\text{-}C_3H_7O)_2PS$ | 1·0176 | 1·4425 | 58·8 | 6·7 | 386–92 |
| $(C_2H_5O)(n\text{-}C_4H_9O)_2P$ | 0·9330 | 1·4285 | 61·2 | $(C_2H_5O)(n\text{-}C_4H_9O)_2PS$ | 0·9969 | 1·4486 | 67·9 | 6·5 | 386–92 |
| $(C_2H_5O)(\mathit{iso}\text{-}C_4H_9O)_2P$ | 0·9270 | 1·4258 | 61·4 | $(C_2H_5O)(\mathit{iso}\text{-}C_4H_9O)_2PS$ | 0·9942 | 1·4450 | 67·9 | 6·5 | 386–92 |
| $(C_2H_5O)(\mathit{iso}\text{-}C_5H_{11}O)_2P$ | 0·9200 | 1·4315 | 70·5 | $(C_2H_5O)(\mathit{iso}\text{-}C_5H_{11}O)_2PS$ | 0·9881 | 1·4530 | 77·1 | 6·6 | 386–92 |
| $(n\text{-}C_4H_9O)(CH_3O)_2P$ | 1·0010 | 1·4215 | 42·1 | $(n\text{-}C_4H_9O)(CH_3O)_2PS$ | 1·1144 | 1·4545 | 48·1 | 6·0 | 386–92 |
| $(n\text{-}C_4H_9O)(C_2H_5O)_2P$ | 0·9561 | 1·4262 | 52·0 | $(n\text{-}C_4H_9O)(C_2H_5O)_2PS$ | 1·0354 | 1·4502 | 58·6 | 6·6 | 386–92 |
| $(n\text{-}C_4H_9O)(\mathit{iso}\text{-}C_5H_{11}O)_2P$ | 0·9050 | 1·4350 | 80·1 | $(n\text{-}C_4H_9O)(\mathit{iso}\text{-}C_5H_{11}O)_2PS$ | 0·9695 | 1·4544 | 80·7 | 6·6 | 386–92 |
| $CH_3P(OC_2H_5)_2$ | 0·9050 | 1·4153 | 37·6 | $CH_3PS(OC_2H_5)_2$ | 1·0554 | 1·4623 | 43·7 | 6·1 | 391, 396, 397 |
| $CH_3P(n\text{-}C_4H_9O)_2$ | 0·8902 | 1·4348 | 56·2 | $CH_3PS(n\text{-}C_4H_9O)_2$ | 0·9858 | 1·4618 | 62·4 | 6·2 | 391, 397–400 |
| $C_2H_5P(CH_3O)_2$ | 0·9515 | 1·4210 | 32·5 | $C_2H_5PS(OCH_3)_2$ | 1·1017 | 1·4722 | 39·2 | 6·7 | 401, 402 |
| $C_2H_5P(C_2H_5O)_2$ | 0·9170 | 1·4217 | 41·5 | $C_2H_5PS(OC_2H_5)_2$ | 1·0331 | 1·4593 | 48·2 | 6·7 | 396, 397, 401–4 |
| $C_2H_5P(n\text{-}C_3H_7O)_2$ | 0·8978 | 1·4298 | 51·2 | $C_2H_5PS(n\text{-}C_3H_7O)_2$ | 0·9990 | 1·4620 | 57·8 | 6·2 | 399, 401–3 |
| $C_2H_5P(\mathit{iso}\text{-}C_3H_7O)_2$ | 0·8844 | 1·4169 | 50·6 | $C_2H_5PS(\mathit{iso}\text{-}C_3H_7O)_2$ | 0·9782 | 1·4521 | 57·9 | 7·3 | 401, 402 |
| $C_2H_5P(n\text{-}C_4H_9O)_2$ | 0·8924 | 1·4361 | 60·4 | $C_2H_5PS(n\text{-}C_4H_9O)_2$ | 0·9718 | 1·4577 | 66·8 | 6·4 | 399, 401–3 |
| $C_2H_5P(C_6H_5O)_2$ | 1·1050 | 1·5660 | 72·6 | $C_2H_5PS(OC_6H_5)_2$ | 1·1811 | 1·5771 | 78·0 | 5·4 | 402 |
| $n\text{-}C_3H_7P(OC_2H_5)_2$ | 0·9029 | 1·4275 | 46·7 | $n\text{-}C_3H_7PS(OC_2H_5)_2$ | 1·0168 | 1·4606 | 52·9 | 6·2 | 395, 400, 403 |
| $n\text{-}C_3H_7P(n\text{-}C_3H_7O)_2$ | 0·8917 | 1·4323 | 55·9 | $n\text{-}C_3H_7PS(n\text{-}C_3H_7O)_2$ | 0·9871 | 1·4608 | 62·2 | 6·3 | 403 |
| $n\text{-}C_3H_7P(n\text{-}C_4H_9O)_2$ | 0·8844 | 1·4389 | 65·4 | $n\text{-}(C_3H_7)PS(n\text{-}C_4H_9O)_2$ | 0·9702 | 1·4623 | 71·40 | 6·0 | 382, 399, 405 |
| $n\text{-}C_4H_9P(C_2H_5O)_2$ | 0·8963 | 1·4308 | 51·3 | $n\text{-}C_4H_9PS(C_2H_5O)_2$ | 1·0015 | 1·4617 | 57·6 | 6·3 | 399, 400, 403 |
| $n\text{-}C_4H_9P(n\text{-}C_3H_7O)_2$ | 0·8961 | 1·4355 | 60·1 | $n\text{-}C_4H_9PS(n\text{-}C_3H_7O)_2$ | 0·9791 | 1·4620 | 66·8 | 6·7 | 403 |
| $n\text{-}C_4H_9P(n\text{-}C_4H_9O)_2$ | 0·8845 | 1·4417 | 69·3 | $n\text{-}C_4H_9PS(n\text{-}C_4H_9O)_2$ | 0·9714 | 1·4635 | 75·5 | 6·2 | 399, 403, 405 |

bonds. This is illustrated by the data given in Table LVII, which shows the bond refraction of the P=S bond as derived from data for trivalent phosphorus compounds and the corresponding thiophosphates.

These data give an average P=S bond refraction value of 6·5. Various summaries of the atomic, molecular and bond refractions for phosphorus have been given.[406–8] Representative values are shown in Table LVIII.

*Table LVIII.—Bond Refractions for Various Phosphorus Bonds*[408]

| Bond | $R_D$ | Bond | $R_D$ |
|---|---|---|---|
| P—H | 4·27 | P—S | 7·31 |
| P—C | 3·64 | P—Cl | 8·79 |
| P—N | 3·46 | P=Se | 9·95 |
| P—O | 3·12 | P—Br | 12·05 |
| P—F | 3·63 | P=S | 6·3 |
| P—Si | 5·29 | P=O | −1·22 |

Values of bond refractions for several non-phosphorus bonds have been reported.[409] These may be used in conjunction with the values in Table LVIII to estimate molar refractivities of phosphorus compounds for which experimental data are not available.

## MISCELLANEOUS PHYSICAL PROPERTIES

### Thermal Conductivity

The thermal conductivities of liquid and supercooled white phosphorus have been measured at temperatures up to 80°C., with the following results (Table LIX):

*Table LIX.—Thermal Conductivity of White Phosphorus*[410]

| Temp. (°C.) | Thermal conductivity $\lambda \times 10^3$ g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ |
|---|---|
| 16 | 1·0015 |
| 20 | 1·0130 |
| 25 | 1·1246 |
| 31 | 1·1980 |
| 33 | 1·2120 |
| 35 | 1·4160 |
| 36 | 1·4725 |
| 37 | 1·5293 |
| 40 | 1·6240 |
| 50 | 1·7820 |
| 60 | 1·9556 |
| 69 | 2·1985 |
| 80 | 2·3125 |

Later results for solid and liquid white phosphorus in the range 25–60°C., obtained by a similar method, are in broad agreement with the values in Table LIX. Simple 'quasi-lattice' theories predict thermal conductivities in good agreement with experimental values.[477]

The thermal conductivity of mono-, di and tetratomic phosphorus has been estimated for the ground state at 1 atm. pressure for temperatures from 100° to 5000°K. These calculations are based on the Lennard-Jones potential and the following equation:

$$\lambda = \frac{\eta R}{M}\left[3{\cdot}75 + 1{\cdot}32\left(\frac{C_p}{R} - \frac{5}{2}\right)\right]$$

where $\lambda$ is the thermal conductivity, $R$ is the gas constant, $C_p$ is the heat capacity, $M$ is molecular weight and $\eta$ is the viscosity in poises.[411] Selected values are given in Table LX.

*Table LX.—Thermal Conductivity of Phosphorus Vapour*[411]

| Temp. (°K.) | Conductivity $\lambda \times 10^6$ (g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$) | | |
|---|---|---|---|
| | P | $P_2$ | $P_4$ |
| 200 | 10·8 | 7·5 | 7·4 |
| 300 | 15·6 | 11·5 | 12·7 |
| 400 | 20·7 | 16·1 | 18·1 |
| 500 | 25·9 | 20·7 | 23·7 |
| 600 | 31·2 | 25·3 | 29·2 |
| 700 | 36·4 | 30·1 | 36·6 |
| 800 | 41·5 | 34·5 | 39·9 |
| 900 | 46·5 | 38·9 | 45·1 |
| 1000 | 51·3 | 43·2 | 50·2 |
| 1200 | 60·4 | 51·2 | 59·6 |
| 1400 | 69·0 | 58·8 | 68·5 |
| 1600 | 77·2 | 66·4 | 76·9 |
| 1800 | 85·2 | 72·5 | 84·7 |
| 2000 | 93·2 | 78·8 | 92·3 |
| 2200 | 101·4 | 84·9 | 99·4 |
| 2400 | 109·9 | 90·7 | 106·2 |
| 2600 | 118·7 | 96·2 | 112·8 |
| 2800 | 128·2 | 101·7 | 119·1 |
| 3000 | 137·6 | 107·0 | 125·2 |
| 3200 | 147·5 | 112·0 | 131·1 |
| 3400 | 157·6 | 117·0 | 136·9 |
| 3600 | 167·8 | 121·9 | 142·4 |
| 3800 | 178·2 | 126·6 | 147·9 |
| 4000 | 188·4 | 131·3 | 153·2 |
| 4200 | 198·6 | 136·0 | 158·4 |
| 4400 | 208·6 | 140·6 | 163·6 |
| 4600 | 218·2 | 145·0 | 168·6 |
| 4800 | 227·5 | 149·5 | 173·5 |
| 5000 | 236·5 | 154·0 | 178·3 |

## Viscosity

The viscosity of mono-, di- and tetratomic phosphorus has been calculated[411] from the expression

$$\eta = \frac{26{\cdot}693\sqrt{MT}}{\sigma^2 \Omega}$$

where $\eta$ is viscosity in poises, $M$ is molecular weight, $T$ is absolute temperature, $\sigma$ the collision diameter in Ångström units and $\Omega$ is the reduced collision integral. Values of the last parameter have been tabulated.[412] Selected viscosity data are given in Table LXI.

## Electronegativity and Bond Properties

Values of bond distances, bond energies and electronegativity differences quoted by Van Wazer[50] are given in Table LXII. The bond energy values should be compared with the more recent values discussed on pages 204–208 above.

The force constant for the P–H bond is reported to be $3{\cdot}10 \times 10^5$ dynes cm.$^{-1}$ [413]

## Spectroscopic Properties

The residual ray or reststrahlen frequency of phosphorus has been calculated[414] from Lindemann's equation

$$\nu = 2{\cdot}8 \times 10^{12} \sqrt{\frac{Tm}{MV^{2/3}}}$$

*Table LXI.—Calculated Viscosity of Phosphorus Vapour*[411]

| Temp. (°K.) | Viscosity $\eta \times 10^6$ (poises) | | |
|---|---|---|---|
| | P | $P_2$ | $P_4$ |
| 200 | 45 | 45·1 | 49·6 |
| 300 | 64·8 | 64·9 | 71·0 |
| 400 | 85·9 | 86·1 | 93·7 |
| 500 | 107·7 | 108 | 117·3 |
| 600 | 129·7 | 130 | 141·3 |
| 700 | 151·3 | 151·7 | 165·1 |
| 800 | 172·5 | 173 | 188·5 |
| 900 | 193·2 | 193·8 | 211·5 |
| 1000 | 213·3 | 213·8 | 233·9 |
| 1200 | 251·2 | 251·9 | 276·7 |
| 1400 | 286·5 | 287·3 | 316·6 |
| 1600 | 319·7 | 320·6 | 354·2 |
| 1800 | 351·1 | 352·1 | 389·8 |
| 2000 | 381·0 | 382·0 | 423·6 |
| 2200 | 409·5 | 410·6 | 456·0 |
| 2400 | 436·8 | 437·9 | 487·0 |
| 2600 | 463·0 | 464·2 | 516·8 |
| 2800 | 488·4 | 489·7 | 545·5 |
| 3000 | 512·8 | 514·2 | 573·4 |
| 3200 | 536·5 | 532·9 | 600·3 |
| 3400 | 559·5 | 561·0 | 626·3 |
| 3600 | 581·9 | 583·5 | 651·7 |
| 3800 | 603·8 | 605·4 | 676·5 |
| 4000 | 625·3 | 627·0 | 700·7 |
| 4200 | 646·3 | 648·1 | 724·4 |
| 4400 | 667·0 | 668·8 | 747·7 |
| 4600 | 687·3 | 689·1 | 770·6 |
| 4800 | 707·2 | 709·1 | 793·1 |
| 5000 | 726·7 | 728·7 | 815·2 |

*Table LXII.—Bond Distances, Bond Energies and Electronegativity in Phosphorus Compounds*[50]

| Bond A–B | Calc. $\sigma$—bond distance (A.) corrected for ionic shortening | | Bond energy[91] (kcal. mole$^{-1}$) | Electronegativity difference ($A_A$–$B_B$)[91] |
|---|---|---|---|---|
| | Reference 90 | Reference 91 | | |
| P–H | 1·46 | 1·426 | 77 | 0·05 |
| P–C | 1·83 | 1·865 | 62 | 0·45 |
| P–Si | 2·25 | 2·25 | 51 | 0·25 |
| P–Ge | 2·30 | 2·31 | 46 | 0·25 |
| P–N | 1·76 | 1·76 | 50 | 0·90 |
| P–P | 2·20 | 2·21 | 50 | 0·00 |
| P–As | 2·31 | 2·34 | 44 | 0·05 |
| P–O | 1·71 | 1·688 | 84 | 1·35 |
| P–S | 2·10 | 2·121 | 55 | 0·45 |
| P–Se | 2·23 | 2·27 | 48 | 0·40 |
| P–F | 1·65 | 1·612 | 114 | 1·75 |
| P–Cl | 2·01 | 2·027 | 77 | 1·00 |
| P–Br | 2·18 | 2·191 | 63 | 0·80 |
| P–I | 2·38 | 2·420 | 48 | 0·50 |

where $T_m$°K. is the melting point, $M$ is molecular weight and $V$ is molecular volume. $\nu$ must be divided by the velocity of light to convert it to a frequency in wave-numbers. The value of $\nu$ is given as 27·5 cm.$^{-1}$ as compared with an observed value of 36 cm.$^{-1}$ However, although the calculated value appears to apply to monatomic phosphorus, it is not clear whether the calculation applies to white or red phosphorus. Also, the figure 27·5 cm.$^{-1}$ does not agree with those previously reported (Mellor, I, 829) for either variety of phosphorus, even when allowance is made for the factor $3{\cdot}08 \times 10^{12}$ instead of $2{\cdot}8 \times 10^{12}$. If the calculation is made for tetratomic white phosphorus a frequency of 36·6 cm.$^{-1}$ is obtained.

Molecular vibration frequencies have been calculated[415] for the $P_2$ and other diatomic molecules containing phosphorus, using the equation

$$\nu(\text{cm.}^{-1}) = 3959{\cdot}4 \sqrt{\frac{K}{\mu r^3}}$$

where $\mu$ is the reduced mass in atomic mass units, $r$ is the interatomic distance in A. and $K$ is a constant. The calculated and observed values are given in Table LXIII.

*Table LXIII.—Calculated and Observed Molecular Frequencies of Diatomic Phosphorus Molecules*[415]

| Molecule | $K$ | $r$(A.) | $\nu$ (cm.$^{-1}$) | |
|---|---|---|---|---|
| | | | Calculated | Observed |
| $P_2$ | 3·670 | 1·894 | 739 | 780 |
| PC | 3·345 | 1·562 | 1261 | 1240 |
| PN | 3·345 | 1·491 | 1281 | 1337 |
| PO | 3·345 | 1·449 | 1279 | 1231 |

A relation between the energy of the ground state of the $P_4$ molecule and the temperature of melting has been discussed with reference to the hole theory of liquids.[416]

## Parachor and Thermochor

The average value of the atomic parachor of phosphorus was given originally as 37·7.[417] Later values have been given as 39·2[418] and 40·5,[419] of which the last appears to be the more generally accepted.[420] On the assumption that bond constants in a molecule should remain unchanged and that the parachor alters with the valency state of an atom, values of 37·1 and 18·3 respectively have been calculated for the atomic parachor of trivalent and pentavalent phosphorus.[421] Similar values were obtained by comparing atoms in the same iso-steric state, i.e., containing equal numbers and kinds of complete electron shells, lone pairs and bonding electrons.[422]

Much higher values, 73·5[423] and 70·5,[424] have been reported for the atomic parachor. These values are based on the observation[423] that, for elements of the same electron configuration around the central nucleus, an increase of one unit in the positive charge on the nucleus lowers the atomic parachor by a constant amount of 5·7. Molecular parachor values may be calculated from atomic parachors by simple addition and subtracting 19 for every bond in the molecule, irrespective of whether this is a single, double, triple or a co-ordinate bond. Parachor values derived in this way for phosphorus compounds are somewhat nearer the observed parachors than those calculated according to the procedure of Sugden. The $P_4$ molecule, however, gives a value of 170[425] as compared with the observed figure of 204·8.[234, 235]

Several other methods of calculating the parachor of the $P_4$ molecule have been examined. The molecular volume $V$ of $P_4$ at absolute zero is 61·6 ml.[175] and the relationship $V = 0{\cdot}346\,P$ gives a value of 178 for the parachor, $P$.[425]

By eliminating the surface tension term in the Sugden equation[426]

$$P = \frac{M\gamma^{1/4}}{D-d}$$

and a modified Eötvös equation[427]

$$\gamma\left(\frac{M}{D-d}\right)^{2/3} = k(T_c-T)$$

the equation

$$\left(\frac{D-d}{M}\right)^{10/3} P^4 = k(T_c-T)$$

is obtained, where $M$ is molecular weight, $T_c$ is critical temperature in °K., $T$ the temperature at which the parachor is determined, $D$ and $d$ are the densities of liquid and gas, respectively, and $k$ is a constant. This constant $k$ has a value of 2·09 for spherical or near-spherical unassociated molecules. A plot of $(D-d)^{10/3}$ against $T$ gives a straight line of slope $-kM^{10/3}/P^4$ from which the parachor can be easily calculated. Using published values[176, 177] for the density of liquid white phosphorus between 45° and 80°C. a parachor value of 205·9 is obtained.[425] Density measurements at temperatures between $-195°$ and $+40°$C.[175, 178] for solid phosphorus give 203·2 for the parachor.

The expression[425]

$$P = 2{\cdot}09^{1/4}\, T_c^{1/4} V_0^{5/6}$$

where $T_c$ is the critical temperature (968°K.) and $V_0$ is the molecular volume of the $P_4$ molecule at 0°K. (61·6 ml.) gives a parachor of 208. The compressibility $X$ is related to the parachor by the equation[428]

$$P = \frac{M}{21(D-d)\, X^{1/6}}$$

where $M$ is the molecular weight. Using a compressibility of $20{\cdot}3 \times 10^{-12}$ cm.$^2$ dyne$^{-1}$ for white phosphorus (Mellor, VIII, 759), the parachor is 197.

The term 'thermochor' has been proposed[429] for the property given by the equation

$$[T] = V^{5/6} T^{1/4}$$

where $[T]$ is the thermochor and $V$ is the molecular volume at the boiling point, $T$°K.; the parachor is 1·055 times the thermochor. These relationships give a parachor of 199·5 for white phosphorus.[430]

## Molecular and Critical Volumes

The density of liquid phosphorus at 580° to 680°C. is given in Table LXIV.

*Table LXIV.—Density of Liquid Phosphorus at High Temperature*[431]

| Temp. (°C.) | Density (g. ml.$^{-1}$) |
|---|---|
| 580 | 1·16 |
| 600 | 1·12 |
| 620 | 1·09 |
| 640 | 1·07 |
| 650 | 1·04 |
| 680 | 0·96 |

The molecular volume of the $P_4$ molecule, based on the above data, varies as shown in Fig. 16, which also includes data for red and black phosphorus.[431] The volume expansion of red phosphorus on melting is unusually large. This indicates a complete change in the structure on melting.[432] The figures give a critical volume of 133 ml. for the $P_4$ molecule at a critical temperature of 695°C.

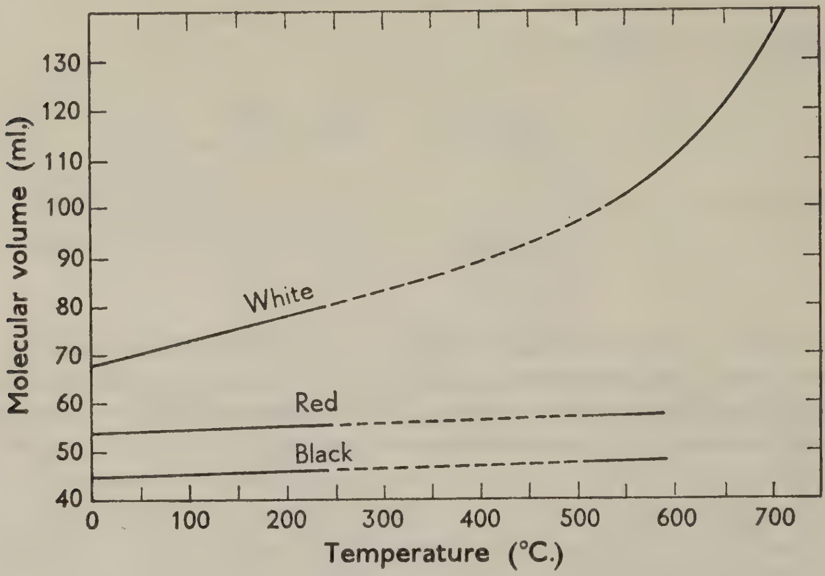


FIG. 16.—Molecular volume of phosphorus

## Other Properties

The velocity of condensation of phosphorus vapour on the solid is a linear function of the temperature difference between the solid and vapour. The rates of condensation

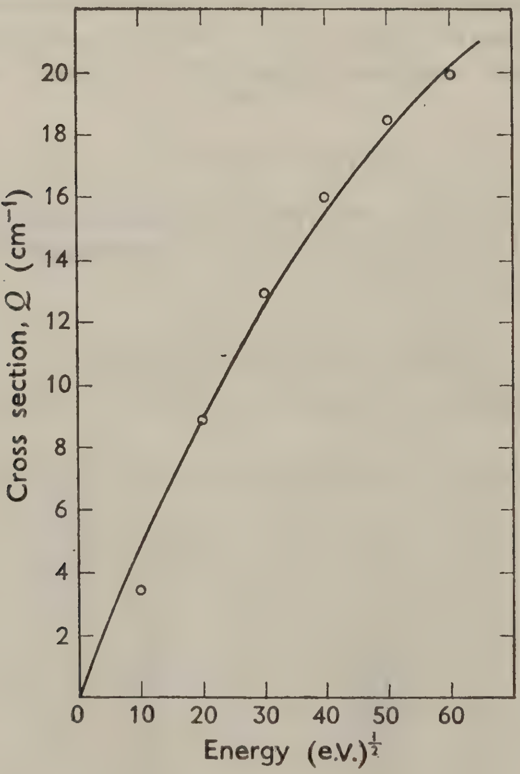


FIG. 17.—Detachment cross-section of $P^-$ ions

in mm. hr.$^{-1}$ are 0·0015, 0·0060, 0·025 and 0·030, respectively, for temperature differences of 0·037°, 0·15°, 0·45° and 0·76°C.[433]

The detachment cross-section $Q$ cm.$^{-1}$ for inelastic collisions, in a neon atmosphere, between negative ions and atoms of phosphorus according to the equation

$$P^- + Ne \rightarrow P + Ne + e - 0{\cdot}3 \text{ e.v.}$$

has been measured[434] with the results shown in Fig. 17.

Phosphorus depresses the freezing point of the platinum metals and a eutectic phase has been observed in rhodium– and ruthenium–phosphorus alloys containing 0·5% P.[435]

Red phosphorus inhibits the rapid crystallization of amorphous sulphur at room temperature. Measurements of the elasticity of sulphur stabilized with 0·8 to 10% of phosphorus indicate a molecular weight of between 18,000 and 73,000 for the $\mu$-phase.[436]

## THE ATOMIC WEIGHT OF PHOSPHORUS

The early work on the atomic weight of phosphorus has previously been discussed (Mellor, VIII, 801). In 1925 the International Union of Pure and Applied Chemistry adopted an atomic weight of 31·027 for phosphorus[437] (oxygen 16). This was based on values of 31·04, 31·027 and 31·018 derived from the ratios $3AgBr:Ag_3PO_4$, $3AgBr:PBr_3$ and $3AgCl:PCl_3$, respectively.[438–40] This value was accepted by the American Chemical Society,[441] but was changed to 31·02 in 1929 because the third decimal place was considered unreliable.[442] The same view was taken by the German Chemical Society.[443]

In the same year, the British Chemical Society considered that the best value for phosphorus was 30·982, the last figure being somewhat uncertain.[444] This value was based largely on measurements made by Aston using the mass spectrograph.[21, 445–6] Observations on the compressibility and density of phosphine confirmed this, giving an atomic weight of 30·977.[447] The reproducibility of this was estimated to be 1 part in 10,000.[448]

The discovery of the isotopes of oxygen in 1929[449–50] resulted in the adoption of two atomic weight scales. On the physical scale, atomic weights were referred to the $^{16}O$ isotope of mass exactly 16. On the chemical scale the standard was naturally-occurring oxygen, the atomic weight of which was defined as 16·0000. Because of the existence of isotopes of masses 16, 17 and 18 in naturally-occurring oxygen, its atomic weight is greater than 16. Consequently, atomic weights based on 'chemical' oxygen are smaller than those referred to 'physical' oxygen. These two scales required the use of a conversion factor derived from measurements of the relative abundance of the three isotopes in naturally-occurring oxygen. For a number of years there was uncertainty as to the magnitude of this factor and some confusion arose over atomic weight values on the two scales. Babcock[451] and Naudé[452] obtained a conversion factor of 1·000125, a value used later by the International Union of Chemistry.[453–4] Mecke and Childs[455] found that the ratio $^{16}O:^{18}O:^{17}O$ was 630:1:0·2 which gave $16{\cdot}0035 \pm 0{\cdot}0003$ for the atomic weight of chemical oxygen and a conversion factor of 1·00022. The ratio $^{18}O:^{17}O = 5:1$ was generally accepted, but the $^{16}O:^{18}O$ ratio was reported to have various values. Aston[456] obtained an approximate value of 536:1 which gives an oxygen atomic weight of 16·0041 and a conversion factor of 1·000256. A later measurement[457] gave a ratio of $(514 \pm 13):1$, corresponding to $O = 16{\cdot}0043$ and a conversion factor of 1·00027. What are probably the most reliable data[458] give the isotopic composition of oxygen as $^{16}O$ 99·76%, $^{17}O$ 0·04% and $^{18}O$ 0·20%. Allowing for the packing fractions,[459] $^{17}O = +2{\cdot}7 \times 10^{-4}$ and $^{18}O = +2{\cdot}1 \times 10^{-4}$, the atomic weight of chemical oxygen is 16·00441 which gives a conversion factor of 1·000275. This value has been accepted since 1938.[460]

During the decade following 1929 evidence accumulated,[461–2] which showed that the value of 31·02 for the chemical atomic weight of phosphorus was too high. Spectrographic measurements indicated a chemical atomic weight of 30·9844[463] or

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30·9836 ± 0·0006.[464] A chemical determination of the ratios $POCl_3$:3Ag and $POBr_3$:3Ag gave atomic weights of 30·978[465–6] and 30·974,[467] respectively, but the latter value was considered to be slightly less certain. A chemical atomic weight of 30·98 was adopted by the International Union of Chemistry in 1939[468–9] and 30·975 in 1951.[470]

Owing to the greater precision in determining atomic weights by spectrographic and similar procedures, and for other reasons, the International Union of Pure and Applied Physics in 1960[471] adopted an atomic weight scale based on $^{12}C = 12{\cdot}0000$. On this basis the atomic weights of phosphorus and naturally-occurring carbon and oxygen are 30·9738, 12·01115 ± 0·00005 and 15·9994 ± 0·00010, respectively.[471–2] The uncertainty in the values for oxygen and carbon is caused by variations in the isotopic compositions of these elements.

With the new atomic weight scale the differentiation into 'physical' and 'chemical' atomic weights no longer applies. A factor is required, however, for converting atomic weights on the old physical scale to those based on the $^{12}C$ scale. This factor is calculated as follows:

On the old physical scale, which is based on $^{16}O = 16{\cdot}0000$, the atomic weight of the $^{12}C$ isotope of carbon is 12·0038150.[20, 24, 48] Dividing this by 12 gives the divisor $1{\cdot}000317917 \pm (17 \times 10^{-9})$ by which the physical atomic weights must be divided to convert them to the $^{12}C$ scale.[471–2] Chemical atomic weights reported since 1939 must be multiplied by 1·000275 before carrying out the above conversion.

It should be noted that the atomic weight of carbon was revised when the change to the $^{12}C$ scale was made, the new value being 12·01115 ± 0·00005.[471] This was due to the observation that naturally-occurring carbon contained between 1·1088% and 1·1151% of the $^{13}C$ isotope,[473] and the mass of this isotope is 13·003354 on the $^{12}C$ scale.[20, 24]

The new atomic weight of oxygen (15·9994) was derived from the isotopic composition of 99·7587% of $^{16}O$, 0·0374% of $^{17}O$ and 0·2039% of $^{18}O$ for naturally-occurring oxygen.[474] On the $^{12}C$ scale the isotopic masses are[48] 15·994915 for $^{16}O$, 16·999134 for $^{17}O$ and 17·999160 for $^{18}O$.

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## SECTION V

# THE CHEMICAL PROPERTIES OF PHOSPHORUS

BY D. R. PECK

Phosphorus forms binary compounds with all the other elements with the exception of the inert gases of the helium group, antimony, bismuth and possibly a few of the rare earths. For these elements either compounds with phosphorus have not been reported, or their existence is doubtful.

The reactions of phosphorus with oxygen and with the halogens are spontaneous at room temperature and highly exothermic. At temperatures below about 250°C. vigorous reactions occur with sulphur and the alkali metals. Phosphides are formed with metallic elements, usually by heating with phosphorus vapour or with red phosphorus. In some of these reactions, e.g. with iron, nickel, copper or platinum, the reacting mass may become incandescent.[1]

Helium is the only inert gas for which any evidence of reaction with phosphorus has been reported. At liquid-air temperatures, under the influence of electron bombardment, helium is absorbed by, or forms an interstitial compound with, phosphorus. The product decomposes suddenly at $-125$°C. with evolution of helium.[2]

## THE REACTIONS OF PHOSPHORUS WITH NON-METALLIC ELEMENTS

### Hydrogen and its Isotopes

Hydrogen is one of the least reactive of the non-metals in that it does not combine directly with phosphorus at normal temperatures and pressure. Atomic hydrogen, however, readily converts phosphorus into phosphine.[3]

The PH molecule does not exist at room temperature but a band at 3400 A., corresponding to a $^3\Pi \rightarrow {}^3\Sigma$ transition, has been observed in the spectra of mixtures of hydrogen and phosphorus vapour.[4-7] The emission spectrum of the $PH^+$ molecule has been observed in a cathode discharge through helium containing phosphorus vapour and hydrogen.[8]

There is no reaction between red phosphorus and hydrogen at 400°C. and only small amounts of phosphine are formed at 550°C.[9] The equilibrium between hydrogen and phosphorus under pressure has been studied,[10] some phosphine being obtained by heating the elements in a closed tube at 360°C.[11] However, very high pressures are necessary to obtain any significant yield of phosphine.[12] From the experimental data the following results have been calculated[13-4]:

$$\begin{aligned} P_4 + 6H_2(g) &= 4PH_3(g) & \Delta H_0^\circ &= 1530 \text{ g.-cal.} \\ P_{(\text{white})} + \tfrac{3}{2}H_2(g) &= PH_3(g) & \Delta G_{298}^\circ &= -3140 \text{ g.-cal.} \end{aligned}$$

The heat of formation of phosphine is uncertain (see Section VI) and $\Delta H_0^\circ = 1530$ g.-cal. is an estimated 'best' value. Using a free energy $\Delta G_{298} = -18{,}370$ g.-cal. for the first of the above reactions, values of the equilibrium constant

$$K = \frac{P_{PH_3}^4}{P_{P_4} \cdot P_{H_2}^6}$$

shown in Table I have been reported.[13]

*Table I.—Equilibrium Constant, $K_{\text{atm.}}$, for the Reaction* $P_4+6H_2(g) = 4PH_3(g)$

| Temp. °K. | Equilibrium constant $K_{\text{atm.}} \times 10^{12}$ |
|---|---|
| 627 | 10 |
| 677 | 5·6 |
| 731 | 2·5 |
| 771 | 1·9 |

Values of $\Delta H°$, $\Delta G°$, $\Delta S°$ and $K_{\text{atm.}}$ for this reaction are given in Table II.

*Table II.—Thermodynamic Properties of Phosphine*[15]

| Temp. °K. | $-\Delta H°$ g.-cal.mole$^{-1}$ | $\Delta G°$ g.-cal.mole$^{-1}$ | $-\Delta S°$ g.-cal.mole$^{-1}$ deg.$^{-1}$ | $K_{\text{atm.}} \times 10^{10}$ |
|---|---|---|---|---|
| 298·1 | 4,300 | 11,590 | 53·3 | 32 |
| 400 | 6,390 | 17,330 | 59·3 | 3·4 |
| 600 | 9,540 | 29,940 | 65·8 | 0·12 |
| 800 | 11,340 | 43,380 | 68·4 | 0·014 |
| 1000 | 12,040 | 57,260 | 69·3 | 0·0031 |
| 1200 | 11,920 | 71,120 | 69·2 | 0·0011 |

Values of the equilibrium constants $K_{\text{I}}=p_{P_4}^{1/4}\cdot p_{H_2}^{3/2}/p_{PH_3}$ for the dissociation

$$PH_3 \rightarrow \tfrac{1}{4}P_{4(\text{vap.})}+\tfrac{3}{2}H_2 \quad (K_{\text{I}} = K^{-0\cdot 25})$$

and $K_{\text{II}}=p_{H_2}^{3/2}/p_{PH_3}$ for the dissociation $PH_3 \rightarrow \frac{1}{4}P_{4(\text{solid})}+\frac{3}{2}H_2$, are given by the equations[309]

$$\begin{aligned} \log_{10} K_{\text{I}} &= -275/T+2{\cdot}46 \log_{10} T-4{\cdot}0\times 10^{-4}T-3{\cdot}74 \\ \log_{10} K_{\text{II}} &= 387/T+0{\cdot}272 \log_{10} T+1{\cdot}32\times 10^{-3}T \\ (T &= 300\text{–}1300°\text{K.}) \end{aligned}$$

For the reaction $\frac{1}{4}P_4(\alpha\text{-white})+\frac{3}{2}H_2=PH_3(g)$ the following values have been calculated[15] for 25°C. and 1 atm.:

$$\Delta H_f^\circ = 2{\cdot}29 \text{ kcal.} \qquad \Delta G_f^\circ = 4{\cdot}34 \text{ kcal.}$$
$$\Delta S_f^\circ = -6{\cdot}88 \text{ g.-cal./deg./mole}$$

Some thermodynamic data for phosphine vapour are given in Table III.

*Table III.—Thermodynamic Properties of Phosphine Vapour*[15]

| Temp. °K. | $H°-H_0^\circ$ g.-cal./mole | $-(G°-H_0^\circ)/T$ g.-cal./mole/deg. | $S°$ g.-cal./mole/deg. |
|---|---|---|---|
| 298·1 | 2,420 | 42·10 | 50·22 |
| 400 | 3,390 | 44·54 | 53·02 |
| 600 | 5,610 | 48·13 | 57·48 |
| 800 | 8,220 | 50·95 | 61·23 |
| 1000 | 11,160 | 53·34 | 64·50 |
| 1200 | 14,360 | 55·45 | 67·42 |
| 1400 | 17,670 | 57·34 | 69·96 |
| 1500 | 19,400 | 58·24 | 71·17 |

The formation of phosphine by the hydrolysis of phosphorus is discussed below. Its preparation by the reaction of phosphides or phosphonium halides with water, and by the thermal decomposition of the lower oxyacids of phosphorus, is described in Section VI (page 272).

Other hydrides of phosphorus have been reported but none of these is formed by direct combination of the elements. The best characterized of these is diphosphine, $P_2H_4$, a water-white liquid,[16] m.p. $-98$°C. and b.p. 51·7°C.[17] Yellow to red solids, corresponding empirically to $P_2H$, $P_5H_2$ and $P_9H_4$, have been described. These compounds result from the decomposition of diphosphine under anhydrous conditions in a sealed system at room temperature. Moisture stabilizes the composition of the product at $P_{12}H_6$.[16] The latter is a yellow powder,[18] stated to be an adsorption compound of phosphine on yellow amorphous phosphorus, formed by the reaction:

$$3P_2H_4 = 4PH_3 + 2P$$

in which 16–20% of the phosphine is adsorbed.[19] The formula has been given as $2PH_3,10P$.[20]

Solid hydrides have been reported to be formed when an electric discharge is passed through a mixture of argon, hydrogen and phosphorus at 25° to 100°C. under pressures of 1 mm.[21] Solid products of formula $(PH)_x$ result from the decomposition of lithium phosphide, LiP, by water[22] or from the reaction of ether solutions of phosphorus trichloride or tribromide and lithium hydride, aluminium hydride or lithium aluminium hydride[23] at temperatures between 0° and $-115$°C.

Liquid polymeric hydrides or phosphanes are said to exist and for these ring $P_nH_n$ or chain $P_nH_{n+2}$ structures are suggested, as well as others ($P_nH_{n-2}$, $P_nH_{n-4}$, etc.) less readily explicable in classical structural terms.[310–2] When heated in nitrogen at 300°C. in the presence of quartz, the chain compounds decompose according to the equation[24]:

$$3P_nH_{n+2} = (n+2)PH_3 + (2n-2)P$$

Deuterium compounds of phosphorus have been prepared, mainly for examination of their spectra. The deuterium analogue of phosphine, $PD_3$, is made by decomposing calcium phosphide with deuterium oxide[25]:

$$Ca_3P_2 + 6D_2O = 2PD_3 + 3Ca(OD)_2$$

or by the reaction of deuterium oxide with phosphorus triiodide.[26] The compound $PH_2D$ has been obtained in an exchange reaction between phosphine and deuterium at temperatures between 20° and 600°C. under pressures of 100–500 mm.:

$$PH_3 + HD \rightleftharpoons PH_2D + H_2$$

The calculated equilibrium constant for this reaction is 1·37 at 0°C. and 1·05 at 700°C.[27] The free radicals $PH_2$ and $PD_2$ have been identified in absorption spectra resulting from the flash photolysis of phosphine and $PD_3$, respectively.[26] The compounds $PHD_2$ and $PH_2D$ have been obtained by equilibrating phosphine with water and deuterium oxide.[28] Deuterio–diphosphine, $P_2D_4$, has been made by reacting calcium phosphide with deuterium oxide.[29] The infra-red and Raman spectra have been examined.[30, 29] Fractional distillation of this material leaves a residue of $P_3H_5$ and other chain $P_nH_{n+2}$ compounds.[24]

Thermodynamic functions have been calculated for $PH_2D$, $PHD_2$,[31–2] $PH_2T$, $PHT_2$,[31] $PD_3$,[33–4] $PT_3$,[35] $PD_2T$ and $PDT_2$,[31] with the results shown in Tables IV–VI. All values are given in g.-cal./deg./mole and refer to the ideal gas state at 1 atm. pressure. Data for phosphine,[33] obtained by the same method of calculation, are given for comparison. Further data for $PH_2D$, $PHD_2$, $PH_2T$, $PHT_2$, $PDT_2$ and PHDT have been reported subsequently.[313] Spectroscopic and other data for some of these compounds have been reported.[25, 28, 36–7]

*Table IV.—Calculated Thermodynamic Functions of* $PH_3$,[33] $PH_2D$[31] *and* $PHD_2$[31] *in g.-cal./deg./mole*

| Temp. °K. | $C_p^\circ$ | | | $\frac{H^\circ-E_0^\circ}{T}$ | | | $S^\circ$ | | | $-\left(\frac{G^\circ-E_0^\circ}{T}\right)$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $PH_3$ | $PH_2D$ | $PHD_2$ | $PH_3$ | $PH_2D$ | $PHD_2$ | $PH_3$ | $PH_2D$ | $PHD_2$ | $PH_3$ | $PH_2D$ | $PHD_2$ |
| 100 | 7·95 | 7·95 | 7·95 | 7·95 | 7·95 | 7·95 | 41·34 | 44·43 | 45·13 | 33·39 | 36·48 | 37·18 |
| 200 | 8·08 | 8·16 | 8·24 | 7·96 | 7·98 | 8·01 | 46·86 | 49·97 | 50·71 | 33·89 | 41·99 | 42·70 |
| 273·16 | 8·54 | 8·78 | 8·96 | 8·05 | 8·10 | 8·20 | 49·44 | 52·59 | 53·42 | 41·39 | 44·49 | 45·23 |
| 298·16 | 8·76 | 9·06 | 9·27 | 8·10 | 8·17 | 8·30 | 50·20 | 53·37 | 54·25 | 42·10 | 45·20 | 45·95 |
| 300 | 8·78 | 9·08 | 9·30 | 8·10 | 8·18 | 8·30 | 50·25 | 53·43 | 54·30 | 42·15 | 45·25 | 46·00 |
| 400 | 9·83 | 10·31 | 10·63 | 8·40 | 8·55 | 8·78 | 52·91 | 56·20 | 57·23 | 44·51 | 47·65 | 48·34 |
| 500 | 10·92 | 11·52 | 11·88 | 8·79 | 9·03 | 9·33 | 55·22 | 58·64 | 59·80 | 46·43 | 49·61 | 50·33 |
| 600 | 11·95 | 12·61 | 12·98 | 9·23 | 9·54 | 9·90 | 57·30 | 60·84 | 62·12 | 48·07 | 51·30 | 52·05 |
| 700 | 12·91 | 13·58 | 13·93 | 9·69 | 10·05 | 10·46 | 59·22 | 62·86 | 64·25 | 49·53 | 52·81 | 53·59 |
| 800 | 13·76 | 14·42 | 14·74 | 10·15 | 10·54 | 10·99 | 61·00 | 64·72 | 66·21 | 50·85 | 54·18 | 55·00 |
| 900 | 14·51 | 15·13 | 15·42 | 10·59 | 11·01 | 11·25 | 62·66 | 66·46 | 68·03 | 52·07 | 55·45 | 56·29 |
| 1000 | 15·16 | 15·74 | 15·99 | 11·02 | 11·46 | 11·70 | 64·23 | 68·10 | 69·71 | 53·21 | 56·64 | 57·77 |

*Table V.—Calculated Thermodynamic Functions of* $PH_2T$,[31] $PHT_2$[31] *and* $PT_3$[33] *in g.-cal./deg./mole*

| Temp. °K. | $C_p^\circ$ | | | $\frac{H^\circ-E_0^\circ}{T}$ | | | $S^\circ$ | | | $-\left(\frac{G^\circ-E_0^\circ}{T}\right)$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $PH_2T$ | $PHT_2$ | $PT_3$ | $PH_2T$ | $PHT_2$ | $PT_3$ | $PH_2T$ | $PHT_2$ | $PT_3$ | $PH_2T$ | $PHT_2$ | $PT_3$ |
| 100 | 7·95 | 7·96 | 7·98 | 7·95 | 7·95 | 7·95 | 45·08 | 46·20 | 44·96 | 37·13 | 38·25 | 37·01 |
| 200 | 8·24 | 8·59 | 9·12 | 7·99 | 8·07 | 8·19 | 50·63 | 51·85 | 50·75 | 42·64 | 43·78 | 42·56 |
| 273·16 | 8·96 | 9·61 | 10·46 | 8·14 | 8·34 | 8·62 | 53·29 | 54·67 | 53·80 | 45·15 | 46·33 | 45·18 |
| 298·16 | 9·27 | 10·00 | 10·92 | 8·23 | 8·46 | 8·79 | 54·10 | 55·53 | 54·73 | 45·87 | 47·07 | 45·94 |
| 300 | 9·30 | 10·02 | 11·90 | 8·23 | 8·47 | 8·80 | 54·15 | 55·59 | 54·79 | 45·92 | 47·12 | 45·99 |
| 400 | 10·63 | 11·57 | 12·65 | 8·66 | 9·05 | 9·56 | 57·00 | 58·68 | 58·19 | 48·34 | 49·63 | 48·63 |
| 500 | 11·88 | 12·93 | 14·07 | 9·18 | 9·70 | 9·68 | 59·51 | 61·42 | 60·52 | 50·33 | 51·72 | 50·84 |
| 600 | 12·98 | 14·06 | 15·21 | 9·73 | 10·33 | 11·05 | 61·78 | 63·88 | 63·84 | 52·05 | 53·55 | 52·79 |
| 700 | 13·93 | 14·99 | 16·09 | 10·26 | 10·94 | 11·71 | 63·85 | 66·13 | 66·25 | 53·59 | 55·19 | 54·54 |
| 800 | 14·74 | 15·73 | 16·77 | 10·77 | 11·49 | 12·30 | 65·77 | 68·17 | 68·44 | 55·00 | 56·68 | 56·14 |
| 900 | 15·42 | 16·34 | 17·30 | 11·25 | 11·99 | 12·83 | 67·54 | 70·05 | 70·46 | 56·29 | 58·06 | 57·63 |
| 1000 | 15·99 | 16·84 | 17·71 | 11·70 | 15·46 | 13·30 | 69·20 | 71·81 | 72·30 | 57·50 | 59·35 | 59·00 |

*Table VI.—Calculated Thermodynamic Functions of* $PD_3$,[33] $PD_2T$[31] *and* $PDT_2$[31] *in g.-cal./deg./mole*

| Temp. °K. | $C_p^\circ$ | | | $\frac{H^\circ-E_0^\circ}{T}$ | | | $S^\circ$ | | | $-\left(\frac{G^\circ-E_0^\circ}{T}\right)$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $PD_3$ | $PD_2T$ | $PDT_2$ | $PD_3$ | $PD_2T$ | $PDT_2$ | $PD_3$ | $PD_2T$ | $PDT_2$ | $PD_3$ | $PD_2T$ | $PDT_2$ |
| 100 | 7·95 | 7·96 | 7·97 | 7·95 | 7·95 | 7·95 | 43·62 | 46·28 | 46·72 | 35·67 | 38·33 | 38·77 |
| 200 | 8·58 | 8·74 | 8·93 | 8·06 | 8·09 | 8·14 | 49·26 | 51·95 | 52·46 | 41·20 | 43·86 | 44·32 |
| 273·16 | 9·62 | 9·88 | 10·17 | 8·33 | 8·41 | 8·51 | 52·37 | 54·84 | 55·42 | 44·04 | 46·43 | 46·91 |
| 298·16 | 10·00 | 10·28 | 10·60 | 8·46 | 8·55 | 8·67 | 52·94 | 55·72 | 56·33 | 44·48 | 47·17 | 47·66 |
| 300 | 10·03 | 10·31 | 10·63 | 8·47 | 8·56 | 8·68 | 53·00 | 55·78 | 56·39 | 44·53 | 47·22 | 47·71 |
| 400 | 11·53 | 11·88 | 12·26 | 9·05 | 9·19 | 9·30 | 56·10 | 58·96 | 59·68 | 47·05 | 49·77 | 50·30 |
| 500 | 12·89 | 13·26 | 13·66 | 9·68 | 9·88 | 10·10 | 58·81 | 61·78 | 62·57 | 49·13 | 51·90 | 52·47 |
| 600 | 14·06 | 14·42 | 14·80 | 10·32 | 10·54 | 10·79 | 61·27 | 64·30 | 65·17 | 50·95 | 53·76 | 54·38 |
| 700 | 15·02 | 15·35 | 15·72 | 10·92 | 11·16 | 11·43 | 63·51 | 66·59 | 67·52 | 52·59 | 55·43 | 56·09 |
| 800 | 15·81 | 16·10 | 16·43 | 11·49 | 11·74 | 12·01 | 65·58 | 68·70 | 69·67 | 54·09 | 56·96 | 57·66 |
| 900 | 16·44 | 16·70 | 16·99 | 12·00 | 12·26 | 12·54 | 67·47 | 70·63 | 71·64 | 55·47 | 58·37 | 59·10 |
| 1000 | 16·95 | 17·18 | 17·44 | 12·47 | 12·73 | 13·01 | 69·23 | 72·42 | 73·46 | 56·76 | 59·69 | 60·45 |

## Boron and Carbon

Red phosphorus and amorphous boron react to form boron phosphide, BP, when heated in a sealed silica tube at 1100° to 1200°C.[38] The pressure is 1–2 atm.[39] The heat of formation from boron and phosphorus:

$$B_{(c)} + P_{(white)} = BP_{(c)}$$

is

$$\Delta H^\circ_{298} = -19{,}900 \text{ g.-cal./mole}$$[40]

The formation of boron phosphide at temperatures up to 10,000°C. and pressures of 15,000 atm. has been studied.[41]

At 1000°C. under 1 mm. pressure, boron phosphide decomposes to form a lower phosphide, $B_{13}P_2$.[42–3] This compound was previously formulated as $B_5P_3$[44] and $B_6P$,[40] both of which appear to be incorrect.[43]

Phosphorus and carbon combine at high temperatures to form the CP molecule[45] which is identified by its band spectrum.[46] Thermodynamic functions for the molecule in the ideal gas state at 1 atm. pressure are given in Table VII. These were calculated from spectroscopic data by statistical mechanical methods. The heats of formation at 0°K. and 25°C., referred to the $\beta$-form of white phosphorus at 0°K. as standard, are $\Delta H^\circ_0 = 107{,}380$ g.-cal./mole and $\Delta H^\circ_{298\cdot15} = 107{,}940$ g.-cal./mole.[47] A yellow carbide, $P_2C_6$, has been reported.[48]

*Table VII.—Calculated Thermodynamic Functions of the* PC *Molecule in g.-cal./deg./mole*[47]

| Temp. °K. | $C^\circ_p$ | $S^\circ$ | $-\left(\frac{G^\circ - H^\circ_0}{T}\right)$ |
|---|---|---|---|
| 273·15 | 7·090 | 51·038 | 44·064 |
| 298·15 | 7·149 | 51·661 | 44·675 |
| 300 | 7·154 | 51·706 | 44·718 |
| 400 | 7·446 | 53·802 | 46·738 |
| 500 | 7·741 | 55·496 | 48·325 |
| 600 | 7·789 | 56·930 | 49·643 |
| 700 | 8·184 | 58·177 | 50·775 |
| 800 | 8·338 | 59·280 | 51·771 |
| 900 | 8·462 | 60·270 | 52·661 |
| 1000 | 8·568 | 61·167 | 53·467 |
| 1200 | 8·765 | 62·747 | 54·886 |
| 1400 | 8·977 | 64·113 | 56·108 |
| 1600 | 9·218 | 65·327 | 57·186 |
| 1800 | 9·483 | 66·428 | 58·153 |
| 2000 | 9·752 | 67·441 | 59·032 |
| 2200 | 10·008 | 68·383 | 59·840 |
| 2400 | 10·237 | 69·264 | 60·589 |
| 2600 | 10·429 | 70·091 | 61·288 |
| 2800 | 10·580 | 70·870 | 61·945 |
| 3000 | 10·692 | 71·604 | 62·565 |
| 3500 | 10·819 | 73·264 | 63·977 |
| 4000 | 10·793 | 74·708 | 65·231 |
| 4500 | 10·688 | 75·974 | 66·355 |
| 5000 | 10·551 | 77·093 | 67·374 |

## Nitrogen

Previous references to the reaction between phosphorus and nitrogen (Mellor, VIII, 122–3) described compounds having P/N mole ratios between 0·6 and 1·1. Yellow phosphorus and nitrogen under the influence of an electric discharge of 4000–15,000 volts at less than 200 mm. pressure give a material having the empirical composition PN. At pressures of less than 20 mm. some red phosphorus is formed and this interferes with the reaction.[49] Phosphorus nitrides have also been obtained using a silent electrical discharge.[50] At 250°C. in the presence of nickel oxide and platinized asbestos as catalyst $P_3N_5$ is said to be formed in this way.[51] At 800°C. it decomposes to give phosphorus and nitrogen, and reacts with water according to the equation[51]:

$$P_3N_5 + 12H_2O = 3H_3PO_4 + 5NH_3$$

The products obtained from an electrical discharge are usually amorphous, but by heating these *in vacuo* or in a stream of nitrogen or ammonia a crystalline product,

$P_3N_5$, is obtained.[52] At about 750°C. *in vacuo*, this material decomposes according to the equation[53]:

$$P_3N_5 = 3PN + N_2$$

The crystalline pentanitride appears to have been confused originally with a polymeric form of the mononitride, $(PN)_n$,[52, 54] obtained by heating phospham, $PN_2H$, *in vacuo* at 450° to 720°C.

The mononitride or its polymeric form is readily obtained by passing phosphorus vapour and nitrogen, at about 1 atm. total pressure, through an electric arc of several thousand volts between tungsten electrodes. As an alternative the gases can be heated at 400° to 500°C. and passed over a tungsten wire heated electrically to about 1500°C.[55] The reaction was originally given as:

$$nP_2(g) + nN_2(g) \rightleftharpoons 2nPN(g) \rightleftharpoons 2(PN)_n(s)$$

but it was later found that at temperatures above 800°C. the nitride is completely dissociated into its elements[56]:

$$(PN)_n \xrightarrow{450°C.} PN \xrightarrow{800°C.} P + N$$

From a calculation of the equilibrium constant[57] the reaction:

$$P_2(g) + N_2(g) = 2PN(g)$$

was found to be favourable for the synthesis of the mononitride at 600° to 800°C. The relevant data are shown in Table VIII and Table IX.

*Table VIII.—Thermodynamic Properties of the* PN *Molecule in the Ideal Gas State at* 1 *atm.*[57]

| Temp. °K. | $C_p$ g.-cal./mole | $S$ g.-cal./mole/deg. | $H-H_0$ g.-cal./mole | $-(G-G_0)$ g.-cal./mole |
|---|---|---|---|---|
| 100 | 6·9544 | 42·824 | 694·6 | 3588 |
| 298·1 | 7·0973 | 50·448 | 2079·1 | 12959·8 |
| 500 | 7·6474 | 54·235 | 3565·1 | 23553·6 |
| 750 | 8·1759 | 57·450 | 5546·6 | 37538·7 |
| 1000 | 8·4774 | 59·842 | 7633·8 | 52209·0 |

*Table IX.—Equilibrium Constants for the Reaction* $P_2(g) + N_2(g) = 2PN(g)$[57]

| Temp. °C. | $K_p e^{+\Delta E_0/RT}$ | $e^{-\Delta E_0/RT}$ | $K_p$ atm. |
|---|---|---|---|
| 800 | 6·09 | 7·87 | 47·9 |
| 900 | 5·94 | 6·58 | 39·1 |
| 1000 | 5·82 | 5·68 | 33·1 |

The above calculation does not agree with the experimental results[56] but the discrepancy can be accounted for by a difference of only a few tenths of an electron-volt in the dissociation energy, $E_0$, of PN.

An investigation into the rate of reaction of the hot-wire synthesis has been made.[58] When equi-atomic mixtures of nitrogen and phosphorus are heated for 42 hr. at 900°C. or for 44 hr. at 950°C. and then quenched at 500°C., no nitrogen is found in the condensed product. Measurements of the degree of dissociation of phosphorus nitride (31·36% N, 67·60% P) at 900°C. give a dissociation energy of 7·1 ± 0·05 e.v.

per PN mole. The equilibrium constant, $K_{\text{atm.}}$, was $10^{-2}$ at 900°C. and 0·20 at 2000°C., giving an average heat of reaction of 14·2 kcal. for the reaction:

$$P_2 + N_2 = 2PN$$

The rate of decomposition of PN is shown in Fig. 1, from which the activation energy of decomposition is 24 kcal./mole. Adding the activation energy of synthesis (7 kcal./mole) gives an apparent activation energy of 31 kcal./mole for the homogeneous synthesis of the PN molecule. This indicates that neither free phosphorus atoms nor free nitrogen atoms represent the activated state or enter into the formation of PN from its elements.

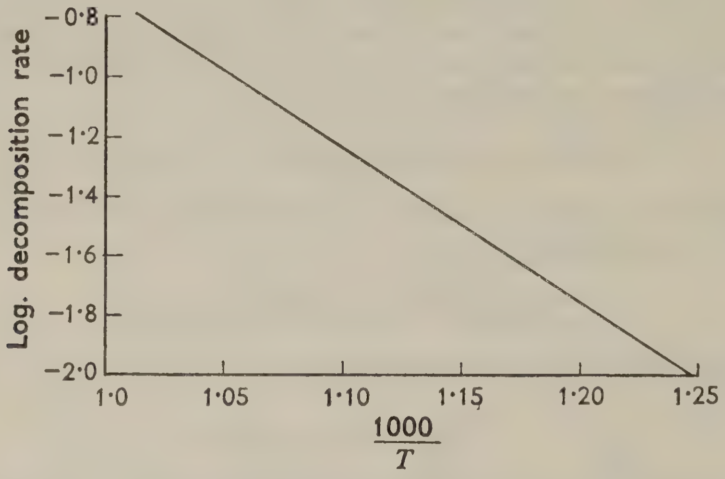


FIG. 1.—Rate of decomposition of PN at 800° to 1000°C.

Observations of the rate of synthesis[58] from phosphorus vapour and nitrogen at atmospheric pressure in the presence of tungsten as catalyst gave a rate constant which agreed with the expression $-\mathrm{d}C_{P_2}/\mathrm{d}t = kC_{P_2}^{1/2}$, where $C_{P_2}$ is the concentration of $P_2$ molecules in moles/c.c. Some data are given in Table X where $k$ is in units of moles$^{1/2}$ c.c.$^{1/2}$ sec.$^{-1}$ cm.$^{-2}$

*Table X.—Rate Constants for the Tungsten-catalyzed Reaction* $P_2 + N_2 = 2PN$ *at Constant Pressure*[58]

| Temp. °C. | Rate constant in moles$^{1/2}$ c.c.$^{1/2}$ sec.$^{-1}$ cm.$^{-2}$ |
|---|---|
| 2080 | $1{\cdot}9 \times 10^4$ |
| 2097 | $2{\cdot}0 \times 10^4$ |
| 2165 | $3{\cdot}5 \times 10^4$ |
| 2212 | $3{\cdot}8 \times 10^4$ |

These data give an activation energy of 59 kcal./mole PN for the catalyzed reaction at temperatures above 1800°C. Since the dissociation energies at 0°K. for $P_2$ and $N_2$ are 58 kcal./g.-atom and 112 kcal./g.-atom respectively, the rate controlling process is the catalyzed dissociation of diatomic phosphorus. This may involve the adsorption of $P_2$ molecules on the tungsten, followed by release from the catalyst surface of phosphorus atoms, which then react with the nitrogen in the gas phase.

A polymerized nitride, $(PN)_n$, is formed when active nitrogen reacts with phosphine at 80° to 290°C. The suggested mechanism is[59]:

$$N + PH_3 = PH_2 + NH$$
$$PH_2 + N = PN + H_2$$

Addition of phosphorus trichloride to liquid ammonia in the presence of nitrogen at $-78$°C. is reported[60] to give an amorphous, pale yellow product having a composition corresponding to PN.

Thermodynamic functions for the PN molecule have been calculated[47] with the results shown in Table XI. The data are for the ideal gas state at 1 atm. The heats of formation at 0°K. and 25°C. referred to the $\beta$-form of white phosphorus are $\Delta H_0 = 22{,}020$ g.-cal./mole and $\Delta H_{298} = 21{,}790$ g.-cal./mole.

*Table XI.—Calculated Thermodynamic Functions of the* PN *Molecule (g.-cal./deg./mole)*[47]

| Temp. °K. | $C_p^\circ$ | $S^\circ$ | $-\left(\frac{G^\circ - H_0^\circ}{T}\right)$ |
|---|---|---|---|
| 273·15 | 7·050 | 49·818 | 42·851 |
| 298·15 | 7·096 | 50·437 | 43·461 |
| 300 | 7·100 | 50·481 | 43·504 |
| 400 | 7·355 | 52·557 | 45·519 |
| 500 | 7·636 | 54·228 | 47·099 |
| 600 | 7·885 | 55·643 | 48·408 |
| 700 | 8·088 | 56·874 | 49·531 |
| 800 | 8·248 | 57·965 | 50·519 |
| 900 | 8·375 | 58·944 | 51·401 |
| 1000 | 8·476 | 59·832 | 52·201 |
| 1200 | 8·623 | 61·392 | 53·606 |
| 1400 | 8·722 | 62·729 | 54·816 |
| 1600 | 8·793 | 63·898 | 55·880 |
| 1800 | 8·846 | 64·937 | 56·830 |
| 2000 | 8·887 | 65·871 | 57·688 |
| 2200 | 8·920 | 66·720 | 58·471 |
| 2400 | 8·948 | 67·498 | 59·191 |
| 2600 | 8·971 | 68·215 | 59·858 |
| 2800 | 8·992 | 68·880 | 60·479 |
| 3000 | 9·010 | 69·501 | 61·060 |
| 3500 | 9·048 | 70·893 | 62·368 |
| 4000 | 9·080 | 72·104 | 63·511 |
| 4500 | 9·108 | 73·175 | 64·526 |
| 5000 | 9·134 | 74·136 | 65·440 |

Phosphorus–nitrogen compounds, such as $P_2NH_3$,[61] $P_4N_6$,[62] $P_3N_5$[63–5] and $P_4(NH_3)$,[65] which are not formed by direct combination, have been described.[66] The properties of these compounds have been discussed in some detail.[66–9] Sections VIII, XI and XVIII should also be referred to.

## Oxygen

White phosphorus combines spontaneously and exothermically with oxygen, and with excess of oxygen forms the pentoxide. Since the discovery of this reaction by Robert Boyle in 1680, oxides with the empirical formulae $P_4O$, $P_2O$, $P_2O_3$, $P_2O_5$ and $P_2O_6$ have been reported[66] (Mellor, VIII, 866), as well as two mixed oxide systems of variable stoicheiometry between $P_4O_{7\cdot7}$ and $P_4O_{9\cdot2}$.[314]

The diatomic molecule PO is unstable under ordinary conditions, but has been identified in band spectra of its vapour.[70–3] Thermodynamic functions for the ideal gas state at 1 atm. pressure have been calculated and are shown in Table XII.[47, 74] The heats of formation at 0°K. and at 298°K. referred to $\beta$-white phosphorus as standard state are $\Delta H_0^\circ = -5710$ g.-cal./mole and $\Delta H_{298\cdot15}^\circ = -5780$ g.-cal./mole. The dissociation energy has been variously given as 5·4 e.v. (125 kcal./mole),[73] 6·07 e.v. (140 kcal./mole)[75] and 6·2 e.v. (143 kcal./mole).[76]

The PO molecule has been observed in the vapour above melts of sodium tripolyphosphate, $Na_5P_3O_{10}$, at temperatures above 700°C.[77]

A number of products exist which are generally referred to as lower oxides of phosphorus. These vary in colour from yellow to red and contain oxygen, possibly hydrogen, and a high percentage of phosphorus. In the earlier literature (Mellor, VIII, 866) there are reports of compounds of the formula $P_4O$[78] and $P_2O$.[79] These have been said[80] to be mixtures of simple compounds, but it is probable that they are complex materials containing P–O, P–P and P–H bonds. $P_4O$ is reported to be present in the reaction products of phosphorus trichloride and either water or aqueous solutions of various salts at temperatures between −20° and −70°C.[81] Its structure is similar to, but more ordered than, that of red phosphorus.[315]

*Table XII.—Calculated Thermodynamic Functions of the* PO *Molecule* (*g.-cal./deg./mole*)[47]

| Temp. °K. | $C_p^\circ$ | $S^\circ$ | $-\left(\frac{G^\circ - H_0^\circ}{T}\right)$ |
|---|---|---|---|
| 273·15 | 7·590 | 52·557 | 45·030 |
| 298·15 | 7·591 | 53·221 | 45·690 |
| 300 | 7·592 | 53·268 | 45·736 |
| 400 | 7·727 | 55·467 | 47·907 |
| 500 | 7·933 | 57·214 | 49·599 |
| 600 | 8·127 | 58·678 | 50·993 |
| 700 | 8·288 | 59·943 | 52·184 |
| 800 | 8·416 | 61·058 | 53·225 |
| 900 | 8·517 | 62·056 | 54·151 |
| 1000 | 8·598 | 62·957 | 54·998 |
| 1200 | 8·715 | 64·536 | 56·451 |
| 1400 | 8·795 | 65·886 | 57·705 |
| 1600 | 8·853 | 67·064 | 58·803 |
| 1800 | 8·897 | 68·109 | 59·780 |
| 2000 | 8·931 | 69·048 | 60·660 |
| 2200 | 8·960 | 69·901 | 61·462 |
| 2400 | 8·984 | 70·682 | 62·198 |
| 2600 | 9·005 | 71·402 | 62·879 |
| 2800 | 9·024 | 72·070 | 63·512 |
| 3000 | 9·040 | 72·693 | 64·104 |
| 3500 | 9·077 | 74·089 | 65·433 |
| 4000 | 9·110 | 75·304 | 66·592 |
| 4500 | 9·141 | 76·378 | 67·621 |
| 5000 | 9·170 | 77·343 | 68·546 |

The autoxidation of suspensions of white phosphorus in carbon tetrachloride gives products which may contain $P_2O$, $(P_2O_3)_n$ or possibly $P_4O_8$.[82]

The oxidation of white phosphorus to the trioxide, $P_4O_6$, is best carried out by burning it at 46° to 50°C. in a quartz tube in a stream of air containing 75% of oxygen and 25% of nitrogen at a pressure of 90 mm. Hg and a flow rate of 30 l./hr.[83] The product is purified by distillation and by irradiating with a mercury arc to convert unchanged white phosphorus to a red form.[84–5] Good yields of the trioxide are also obtained by the oxidation of yellow phosphorus by nitrous oxide at 70 mm. Hg and 550–625°C.[316]

When phosphorus trioxide is heated *in vacuo* it dissociates to a red involatile residue, and a sublimate of large colourless crystals, once thought to be phosphorus tetroxide, $P_4O_8$[86] (Mellor, VIII, 922). This has now been shown to contain two oxide systems of variable stoicheiometry, α-P(III/V) oxide $P_4O_{8\cdot 1}$–$P_4O_{9\cdot 2}$ and β-P(III/V) oxide $P_4O_{8\cdot 0}$–$P_4O_{7\cdot 7}$.[314] The α oxide comprises mixed crystals of the molecules $P_4O_9$ and $P_4O_8$,[317] while the β oxide is a similar mixed crystal of $P_4O_8$ and $P_4O_7$.[318] The structure of the two oxides is discussed further in Section IX.

When a mixture of oxygen and phosphorus pentoxide at a pressure of 1 mm. Hg is passed through a discharge at 3 kv. and 150 ma. between aluminium electrodes, a blue-violet material condenses immediately after the discharge.[87] The product decomposes when heated above 130°C. and is insoluble in chloroform. Its aqueous solution behaves as a peroxyphosphoric acid.[88] In a corona discharge, both the violet and colourless materials are formed. The latter is stable only up to 120°C. and its composition agrees with the formula $P_4O_{11}$.[89] The various oxides of phosphorus are fully discussed in Sections IX and X.

### THE GLOW AND SLOW OXIDATION OF PHOSPHORUS

The oxidation of phosphorus at ordinary temperatures has been studied very extensively since the discovery of the element in 1669. There are two distinct oxidation reactions, both accompanied by the emission of light. When the element oxidizes slowly by reacting in the vapour phase near the solid, it emits a characteristic greenish glow. If rapid oxidation occurs, a yellow flame is produced and this may extend some distance from the solid. The previous observations (Mellor, VIII, 771–81) may be summarized qualitatively as follows.

A greenish glow is observed when white phosphorus is exposed to air or oxygen in the presence of moisture at temperatures of 16° to 30°C., and below atmospheric pressure. No light appears if the oxygen pressure is above about 600 mm. As the pressure decreases, the intensity of the glow increases to a maximum at about 300 mm. pressure and then decreases to zero at zero pressure. Vapours of a number of substances (Mellor, VIII, 775) either stop the glow altogether or necessitate a higher temperature to obtain the same intensity of light. The ignition temperature of the phosphorus is lowered by increasing the water content of the gas. Organic vapours generally raise the ignition temperature (Mellor, VIII, 772). The intensity of the glow varies with the temperature and the partial pressures of water vapour and oxygen. In a closed system of phosphorus and oxygen the rate of decrease in the partial pressure of oxygen increases as $p_{O_2}$ decreases.

In the earlier quantitative measurements of the oxidation of solid white phosphorus it was found that the reaction rate was greatest when only a small amount of water was present. Slower oxidation occurred when very dry or very moist oxygen was used. A partial pressure of 16–20 mm. of water vapour had a very marked inhibiting effect. With oxygen dried by concentrated sulphuric acid the rate of oxidation at 13° to 19°C. agreed with the first order equation $-\mathrm{d}p_{O_2}/\mathrm{d}t = kp_{O_2}$ for pressures between 850 and 2000 mm. At lower pressures $k$ was not constant. When nitrogen was also present, $-\mathrm{d}p_{O_2}/\mathrm{d}t$ passed through a maximum at $p_{O_2} = 250$ mm. This effect was thought to be due to diffusion effects in the gas phase. It was also established that ozone or hydrogen peroxide was formed during the oxidation only if water was present.[90] These data have been examined mathematically.[91]

The formation of ozone, as detected by the liberation of iodine from potassium iodide solution, has been explained by the presence of ultra-violet radiation of wavelength 1200–1800 A. in the spectrum of the glow. This is supported by the observation that ozone is formed during the oxidation of phosphorus trioxide, $P_4O_6$, and the fact that the glow from this reaction oxidizes oxygen. There is, however, evidence that pure $P_4O_6$ does not glow during oxidation and that any glow previously observed was due to the presence of elemental phosphorus in the trioxide.[92] Ozone is also formed in oxygen separated by a quartz window from a glowing phosphorus–oxygen mixture.[93] Some of the radiation has been shown to be emitted by the excited molecule PO.[94] The emission spectrum of the glow shows bands due to three different electronically excited states. One, a state of an unknown physical species of PO, emits a greenish glow in the visible region. Another, the $A^2\Sigma$ state, emits radiation on dropping to the $X^2\Pi$ state. The third, $B^2\Pi$ state radiates by dropping to the ground state. The reaction postulated for the production of these states is[95]:

$$P(^4S) + O(^3P) + PO(X^2\Pi) = PO^* + PO(X^2\Pi)$$

The spectrum of the glow of phosphorus shows a series of lines and bands between 2370 A. and 3420 A.[96–9] and also between 5200 A. and 8000 A.[100–1] Other observations are reported in reference 102.

The effect of nitrogen dioxide on the glow of solid white phosphorus has been determined by measuring the pressure at which the phosphorus begins to glow in the presence of mixtures of the gas with air and oxygen. The pressure, in mm. Hg, is given by the expression $p(a+x) = K$, where $x$ is the ratio $[NO_2]/[O_2]$ and $a$ and $K$ are constants. At 20°C. the values of $a$ and $K$ are 0·00135 and 0·80 respectively for oxygen.[103] It is reported[104] that phosphorus does not[18] glow in pure sulphur dioxide. The pressure at which the glow begins in mixtures of oxygen with sulphur dioxide or hydrogen sulphide increases with temperature. Hydrogen sulphide has a weak inhibiting action similar to that of nitrogen, whereas sulphur dioxide is comparable with benzene and carbon tetrachloride. The pressure limits for both gases are defined by the equation given above.[105] At room temperature the constants in this equation for various gases are as shown in Table XIII. These refer to pressure in mm. Hg and $x$ in volume per cent.

*Table XIII.—Constants in the Equation $p_{\text{mm.}}(a+x)=K$ for the Pressure at which Various Gases Inhibit the Oxidation of White Phosphorus in Air or Oxygen*[106]

| Inhibitor | Constant $a$ | | Constant $K$ | |
|---|---|---|---|---|
| | $O_2$ | air | $O_2$ | air |
| Sulphur dioxide | 23 | — | 1,350 | — |
| Benzene | 21 | 32 | 10,805 | 4912 |
| *cyclo*Hexane | 20 | 14 | 10,107 | 2113 |
| Acetylene | 11·3 | 4·8 | 7,017 | 1249 |
| Methyl*cyclo*hexane | 8·2 | 6·2 | 4,577 | 1023 |
| Ethylene | 1·75 | 0·66 | 1,073 | 177 |
| Propylene | 0·35 | 0·15 | 168 | 26 |
| *cyclo*Hexene | 0·11 | 0·08 | 58 | 9 |
| Isoprene | 0·025 | 0·01 | 20 | 2·6 |
| Iron carbonyl, $Fe(CO)_5$ | 0·0033 | 0·0019 | 1·7 | 0·21 |

The pressure necessary to prevent luminous oxidation at 20°C. in the absence of chemical inhibitors is 588 mm. for oxygen and 1195 mm. for moist air.[107] The inhibiting action of ethylene, chlorine and bromine is less than that of nitrogen dioxide.[108] The inhibiting effect of some compounds has been expressed by an equation of the form:

$$p_{\text{mm.}} = p_0 - Ax$$

where $p_0$ is the pressure which prevents oxidation in pure oxygen, $A$ is a constant and $x$ is the volume percentage of inhibitor in the gas phase.[106, 109] Some data are given in Table XIV.

*Table XIV.—Constants in the Equation $p=p_0-Ax$ for the Inhibition of the Oxidation of Solid White Phosphorus by Oxygen*[106, 109]

| Inhibitor | Temp. °C. | $p_0$ | $A$ |
|---|---|---|---|
| Nitrogen | 15–16 | 670 | 3·6 |
| Hydrogen | 17·5 | 732 | 6·2 |
| Carbon monoxide | 6·5 | 400 | 3·5 |
| Carbon dioxide | 12 | 510 | 4·6 |
| Nitrous oxide | 14 | 480 | 4·25 |
| Chloroform | 20 | 549 | 10·4 |
| Carbon tetrachloride | 15 | 533 | 8·35 |
| | 20 | 678 | 12·45 |
| Ethyl bromide | 17·5 | 540 | 8·0 |
| Ethylene dibromide | 14·5 | 540 | 10·0 |
| Methyl acetate | 18·2 | 543 | 41·5 |

The data for a number of vapours, particularly those of aromatic compounds, agree better with an equation of the form[106–7]:

$$p = p_0 - Ax + Bx^2$$

Phosphorus oxychloride vapour is anomalous in that it catalyzes the glow, the pressure at 20°C. agreeing with the equation:

$$p = \frac{1650}{2{\cdot}1 - x}$$

for the low concentrations investigated.[109]

In the earlier literature (Mellor, VIII, 772) various values were reported for the ignition temperature of phosphorus. More recent data[110] show that the true ignition temperature in dry air is 38·5°C. This value was obtained by determining the lower and upper limits of air pressure between which a phosphorus flame was obtained at various temperatures. The data are given in Table XV, from which it will be seen that the lower pressure limit varies only slightly with temperature, whereas the upper limit increases rapidly as the temperature is raised.

*Table XV.—Pressure Limits in the Hot Flame Oxidation of White Phosphorus*[110]

| Temp. °C. | Lower limit mm. | Upper limit mm. |
|---|---|---|
| 2 | 70 | 75 |
| 7 | 66 | 100 |
| 19 | 65 | 200 |
| 22 | 64 | 300 |
| 25 | 62–64 | 400 |
| 28 | 62–64 | 500 |
| 31·5 | 62–64 | 600 |
| 35·5 | 62 | 700 |
| 38·5 | 60–62 | 760 |
| 41·5 | 60–62 | 800 |
| 47·0 | 60–62 | 900 |
| 50·0 | 60 | — |

These data are shown in Fig. 2, which includes other observations defining the boundary between the glow and flame regions in the oxidation.

Hydrocarbons have a marked influence on the boundaries, the effect varying with temperature. The pressure–composition diagram for these at a temperature of 44·5°C. is shown in Fig. 3.

A change of 10°C. in the temperature considerably alters the shape of the diagram. As the temperature is lowered, the flame region becomes smaller and the region of no reaction shown in Fig. 3 moves to the left.[110]

It is reported[111] that the inflammability, *I*, of a substance is given by the expression:

$$I = \frac{\text{heat of combustion} \times \text{specific heat}}{\text{ignition temperature}}$$

On this basis the inflammability of white phosphorus is 834 and that of the red variety is 128, as compared with 25–35 for hydrogen and 63 for carbon disulphide.

The vapour phase oxidation of white phosphorus has been studied in great detail, and more precise data have been obtained than has been possible in the study of the solid element. In the earlier stages of this work it was found that for a given pressure of phosphorus there is an upper limit to the oxygen pressure, above which only slow oxidation occurs and below which ignition takes place.[112] The upper pressure limit is directly proportional to the pressure of phosphorus vapour[113] and is independent of temperature between −40°C. and +15°C. This pressure has been considered to be the lower limit of explosion[114–5] in mixtures of phosphorus vapour and oxygen.

There is also a lower pressure limit, below which the oxidation is very slow and above which ignition occurs. The lower critical pressure is independent of temperature and is inversely proportional to the pressure of phosphorus vapour and the

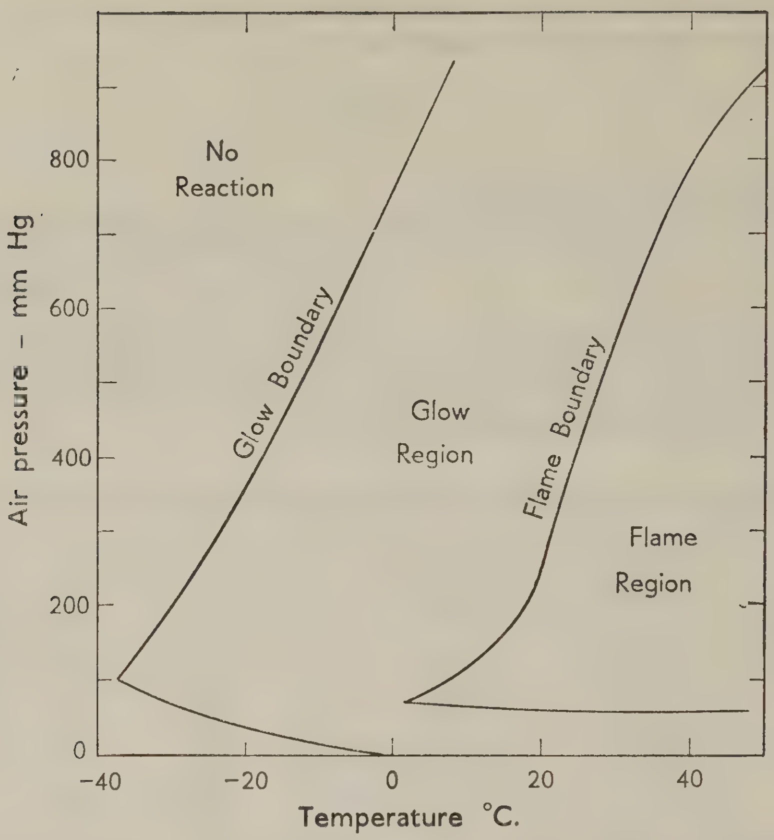


FIG. 2.—The glow and flame regions in the oxidation of solid white phosphorus in air[110]

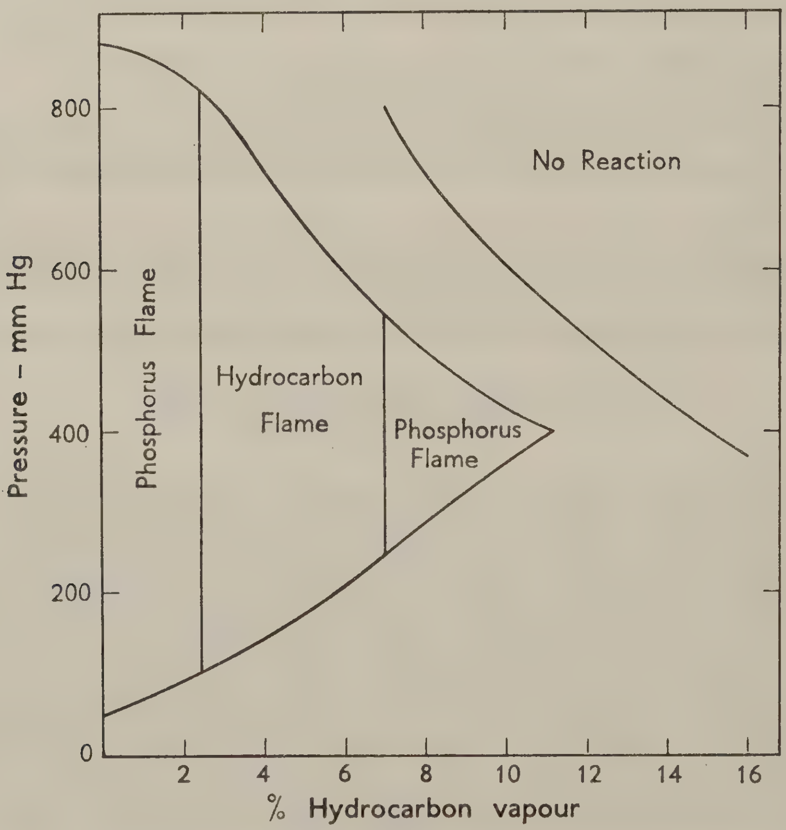


FIG. 3.—The effect of hydrocarbons on the oxidation of solid white phosphorus in air at 44·5°C.[110]

**Refs. p. 264**

square of the diameter of the containing vessel. It is also lowered by the addition of inert gases such as argon. Earlier data[116–7] were in approximate agreement with Semenoff's expression[118]:

$$p_{\mathrm{P}}\, p_{\mathrm{O}} \left(1 + \frac{p_{\mathrm{A}}}{p_{\mathrm{O}}+p_{\mathrm{P}}}\right) d^2 = \text{constant}$$

where $p_{\mathrm{A}}$, $p_{\mathrm{P}}$ and $p_{\mathrm{O}}$ are the pressures of inert gas, phosphorus vapour and the critical pressure of oxygen, respectively, and $d$ is the diameter of the vessel.

The two pressure limits were shown[113] to be limiting cases of a general equation which determines the explosion conditions of phosphorus–oxygen mixtures, i.e.

$$k_1 - p_{\mathrm{P}}\, p_{\mathrm{O}} + k_2 p_{\mathrm{O}}^2 = 0$$

where the constants are $k_1 = 3{\cdot}2 \times 10^{-4}$ and $k_2 = 2{\cdot}8 \times 10^{-5}$. The lower $p_1$ and the upper $p_2$ critical oxygen pressures are then given by:

$$p_1 = \frac{p_{\mathrm{P}} - \sqrt{p_{\mathrm{P}}^2 - 4k_1k_2}}{2k_2} \quad \text{and} \quad p_2 = \frac{p_{\mathrm{P}} + \sqrt{p_{\mathrm{P}}^2 - 4k_1k_2}}{2k_2}$$

This result is shown in Fig. 4, where the curve is derived from the above equations and the points represent the experimental data. Pressures are in mm. Hg and the area inside the curve is the region of fast reaction.[115, 119, 120]

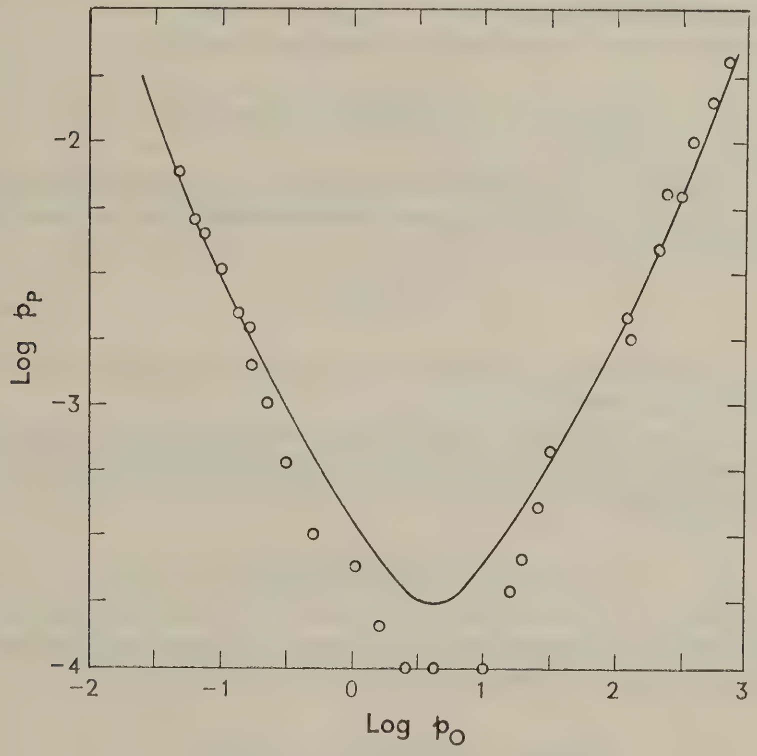


FIG. 4.—Critical pressures in the oxidation of phosphorus vapour

These observations were explained[120–1] by a chain mechanism in which it is considered that oxygen atoms provide the reaction centres. Chain propagation spreads until ignition occurs, unless the chains are terminated by the walls of the containing vessel. The reactions postulated are:

$$\begin{aligned} \mathrm{O_2} &= \mathrm{O + O} \\ \mathrm{O + P_4} &= \mathrm{P_4O} \\ \mathrm{O_2 + P_4O} &= \mathrm{P_4O_2 + O} \end{aligned}$$

Consecutive reactions of $P_4O_2$ could cause chain branching:

$$\begin{aligned} P_4O_2+2(n-1)O_2 &= P_4O_{2n} \\ P_4O_{2n}+O_2 &= P_4O^*_{2n+2} \\ P_4O^*_{2n+2}+O_2 &= P_4O_{2n+2}+2O \end{aligned}$$

where $P_4O^*{}_{2n+2}$ is an activated molecule. The last reaction occurred only when the kinetic energy of the oxygen molecule and the excess energy $\phi$ of the $P_4O^*_{2n+2}$ molecule exceeded 160,000 g-cal. The probability of this is $e^{-E/RT}$ where

$$E = 160{,}000-\phi$$

The chain length $\nu$ at which ignition occurs is $\nu=\frac{1}{2}e^{+E/RT}$. The addition of an inert gas increases the rate of oxidation by hindering the diffusion of the chains to the walls of the vessel, thus increasing the chain length.

The hypothesis that the reaction centres are formed spontaneously in the gas phase has been criticized because it does not explain why the formation of the centres ceases abruptly with small changes in pressure. It seems that the chain theory should be modified in favour of a heterogeneous initiation of inflammability.[122]

A study of the effect of hydrogen, helium, neon, argon, nitrogen, carbon monoxide and dioxide, hydrogen sulphide, nitrous oxide, sulphur dioxide, and the vapours of acetone, acetylene, ethylene, benzene, hexane, methylene chloride and mesitylene on the lower oxidation pressure gives results which agree with Semenoff's equation. This indicates that the inert gas effect should be independent of the nature of the gas. However, the slope of the curve obtained by plotting $1/p_O$ against $1+[p_A/(p_O+p_P)]$ varies with the nature of the gas.[123]

A better approximation is obtained by using the equation:

$$p_P\, p_O \left(1 + \frac{\mu p_A}{p_O+p_P}\right) d^2 = \text{constant}$$

where $\mu$ is the reciprocal of the diffusion coefficient of oxygen through the inert gas. In the upper pressure limit the termination of the chains is in the gas phase and

$$p_O = \frac{k}{a+p_A/p_O}$$

The ratio $k/a$, which should be independent of the inert gas, varies from 350 for acetylene to 800 for isoprene.[124]

Values of $\mu$ have been obtained in two ways. In one of these the acceleration of the chain reaction velocity by an inert gas is measured. If $R_X$ and $R_O$ are the rates with and without the gas, then:

$$\mu = \left(\frac{R_X-R_O}{R_O}\right)\left(\frac{p_O+p_P}{p_X}\right)$$

In the second method the depression of the lower pressure limit on adding an inert gas is measured. For these circumstances:

$$p'_O\, p'_P = p_O\, p_P \left(1 + \frac{\mu p_X}{(p_O+p_P)}\right)$$

where $p'_O$ and $p'_P$ are the pressure limits in the absence of inert gas.[125] Some values of $\mu$ are given in Table XVI.

For hydrogen and deuterium values of $\mu=0{\cdot}10$ and $\mu=0{\cdot}128$, respectively, have been obtained.[126, 125]

Illumination of the vapour with a zinc spark or a mercury arc, at pressures below the lower limit, displaces the latter towards smaller pressures and also causes the reaction between phosphorus vapour and oxygen to occur at below the critical limit. The displacement is a wall effect, said to be due to dissociation of $P_4$ into $P_2$ molecules. Illumination with ultra-violet light raises the upper pressure limit, but this is not a

*Table XVI.—Constants for the Effect of Inert Gases on the Oxidation of Phosphorus Vapour*[125]

| Inert gas | Constant $\mu$ |
|---|---|
| Helium | 0·13 |
| Neon | 0·20 |
| Argon | 0·46 |
| Nitrogen | 0·37 |
| Carbon dioxide | 0·48 |
| Sulphur dioxide | 0·52 |
| Nitrous oxide | 0·46 |
| Chloroform | 0·84 |
| Carbon tetrachloride | 0·84 |

wall effect. The kinetics of the stable oxidation at pressures below the lower limit in the presence of ultra-violet light are represented by the equation:

$$\frac{-\mathrm{d}[O_2]}{\mathrm{d}t} = kI[O_2]^2[P_4]$$

where $k$ is a constant and $I$ is the intensity of illumination. This experimental result does not agree with the prediction of the chain theory of reaction, according to which the rate of reaction should be proportional to the oxygen pressure and the square of the phosphorus vapour pressure. The observed rate equation would result if the production of one of the chain carriers were due to the formation of a lower phosphorus oxide on the walls of the apparatus rather than the dissociation or deactivation of phosphorus molecules by ultra-violet light.[126]

A slow oxidation reaction is induced by platinum or tungsten at 200° to 500°C. at pressures below the lower critical limit. With a platinum filament no glow is emitted and the reaction velocity at 200°C. is proportional to the oxygen pressure. Introduction of argon does not affect the reaction rate. At 500°C. with a tungsten filament the reaction velocity is proportional to both the oxygen and the phosphorus vapour pressures. It is increased by using wider reaction tubes and by adding neon or argon. The rate equation is:

$$-\frac{\mathrm{d}p_O}{\mathrm{d}t} = kp_O\,p_P\left(1 + \frac{\mu p_X}{p_O + p_P}\right)d^2\,\mathrm{e}^{-E/RT}$$

where $d$ is the diameter of the tube, $p_O$, $p_P$, and $p_X$, are the pressures of oxygen, phosphorus vapour and inert gas, respectively, $\mu$ has the values given in Table XVI and the activation energy is $E = 16$ kcal. Silver, gold and molybdenum have a similar effect.[127]

The glow-type oxidation of phosphorus has been explained in terms of branched chain reactions, and this theory accounts for the temperature dependence of the glow limits.[128] A more recent and detailed discussion examines the factors affecting the lower and upper limits of the cool-flame reaction.[129] The proposed scheme for the oxidation is:

| | | |
|---|---|---|
| (1) | $P_4 + O_2 \rightarrow P_4O + O$ | Initiation |
| (2) | $P_4 + O + M \rightarrow P_4O + M$ | Propagation |
| (3) | $P_4O_n + O_2 \rightarrow P_4O_{n+1} + O$ | Chain branching |
| (4) | $O + O_2 + M \rightarrow O_3 + M$ | Termination |
| (5) | $O + X \rightarrow$ stable product | Termination |
| (6) | $O +$ wall $\rightarrow$ adsorption | Termination |

This is a slight modification of the mechanism previously given[128] in that reaction (2), which requires no activation energy, is a three-body process with M as the third atom. The simpler reaction:

$$P_4 + O \rightarrow P_4O$$

involves the liberation of too much energy to explain the observed data.[128] In reaction (3), $n$ can have any integral value between 1 and 9, and the activation energy for reaction (4) is 4·3 kcal./mole. In reaction (5) X is a foreign gas which acts as an inhibitor by reacting with oxygen atoms, e.g. an unsaturated aliphatic hydrocarbon.[129]

The intensity of the glow of phosphorus has been measured with a photo-electric photometer. In oxygen at 40–350 mm. pressure the intensity is approximately constant at temperatures up to 380°C. At room temperatures ozone has no effect at concentrations below 0·14%. At higher concentrations the glow intensity is increased according to the equation:

$$I = 5+2{\cdot}95(x-0{\cdot}14)$$

where $x$ = percentage of $O_3$.

Chlorine and sulphur dioxide decrease the intensity and at high enough concentrations extinguish the glow. Chlorine is much the more effective in this respect, the equations being:

$$\begin{aligned} Cl_2: &\quad I = 6{\cdot}7(1-0{\cdot}433R) \\ SO_2: &\quad I = 4{\cdot}25(1-0{\cdot}009R) \end{aligned}$$

where $R$ is the ratio $Cl_2/O_2$ or $SO_2/O_2$ as measured by the partial pressures.[130]

Investigation of the glow with a photoelectric counter[131] gave results in agreement with the originally proposed reaction mechanism.[118]

The band spectrum of the green flame of phosphorus[132] and the fluorescence and absorption spectra of superheated phosphorus vapour[133] have been investigated. Fluorescent emission has been observed in the 1900–3500 A. region on illuminating the vapour at 600° to 700°C. under 0·1 mm. Hg pressure with aluminium, cadmium and zinc light.[134]

The rate of oxidation of white phosphorus in air at temperatures between 125° and 450°C. shows that the reaction time has relatively little effect on the composition of the products. Table XVII shows the percentages of the various oxides formed at four temperatures.

*Table XVII.—Products obtained in the Air-oxidation of White Phosphorus*[135]

| Oxidation product | % composition at | | | |
|---|---|---|---|---|
| | 125°C. | 250°C. | 350°C. | 450°C. |
| $P_4O$ | 28 | 20 | 10 | — |
| $P_4O_2$ | 0·6–4·7 | 0·9–4·0 | 0·3–0·9 | — |
| $P_4O_6$ | 35 | 19 | 14 | 12 |
| $P_4O_{10}$ | 35 | 59 | 75 | 88 |

The first stage of the oxidation was represented by the equations:

$$\begin{aligned} P_4+O &= P_4O \\ P_4O+O_2 &= P_4O_2+O \\ P_4O_2+O_2 &= P_4O_4 \end{aligned}$$

At low pressure this was followed by:

$$\begin{aligned} P_4O_4 &= 4PO \\ PO+O_2 &= PO_3 \\ PO_3+O_2 &= PO_2+O_3 \\ 2PO_2 &= P_2O_4 \\ P_2O_4+O_3 &= P_2O_5+O_2 \end{aligned}$$

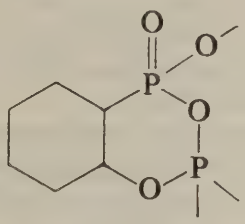
At high pressures $P_4O_4$ reacts with one, two and three molecules of oxygen to give $P_4O_6$, $P_4O_8$ and $P_4O_{10}$, respectively.[135]

The formation of substantial quantities of $P_4O$ has been doubted.[129] This product was not obtained in a previous detailed examination of the oxidation of phosphorus.[92] Careful repetition of this work failed to give any $P_4O$ which could be isolated as a separate product.[129] Later workers have proposed a detailed mechanism along similar lines for the oxidation of phosphorus via the trioxide to the pentoxide.[319]

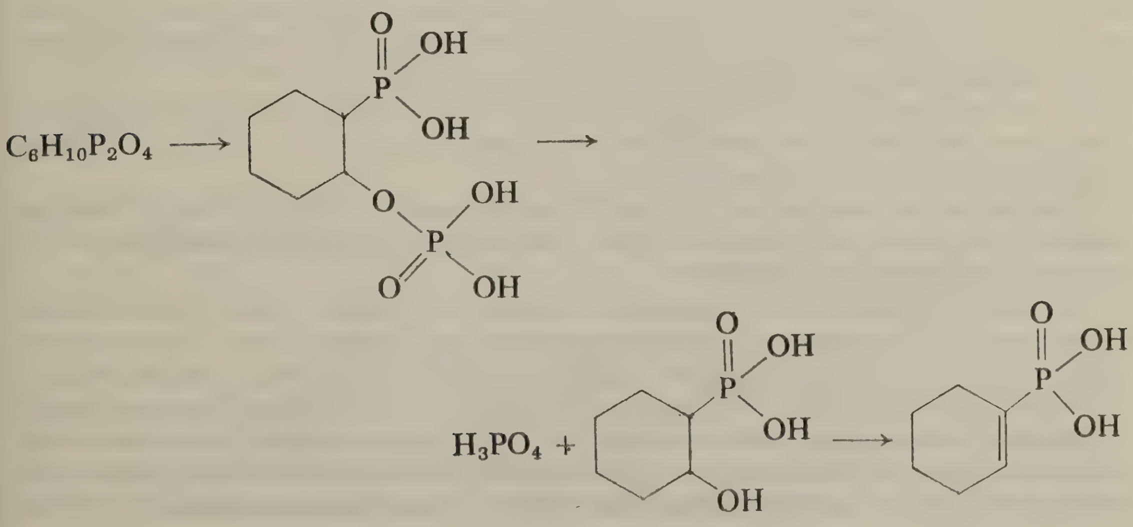
Oxidation of white phosphorus with oxygen at 100°C. in the presence of water vapour gives amorphous yellowish-red products. These contain hydrogen and oxygen, and 87 to 91% of phosphorus. The composition of the product with the lowest phosphorus content corresponds to $(P_4(OH))_n$. These materials are insoluble in water and decompose in an inert atmosphere at 250° to 300°C. to form red phosphorus and pentavalent phosphorus compounds. They oxidize slowly in air to give hypophosphorous acid, phosphorous acid, some phosphoric acid and traces of lower reduced acids of phosphorus.[136]

Orange-coloured products, which contain bromine atoms and may also contain $(P_4(OH))n$, are formed when pentaerythritol is converted to its tetrabromide by refluxing with phosphorus tribromide.[136A]

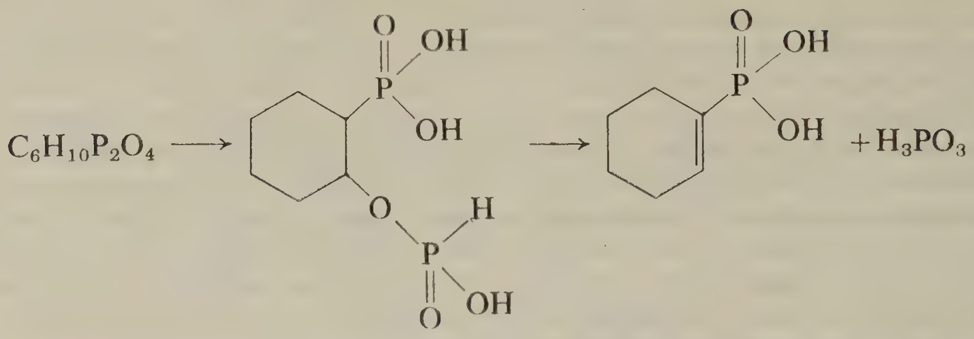
In the presence of olefins the oxidation of benzene solutions of white phosphorus with oxygen at 40° to 50°C. produces organic polymers.[137] The reaction in most cases attains 100% completion with the absorption of two atoms of oxygen to each atom of phosphorus. The oxidation is a free radical process, giving large molecules of kinetic chain length at least 7000. The reaction is inhibited by hydroquinone, but is accelerated by azobis–*iso*butyronitrile. The products are white or light-yellow crystalline solids, which react vigorously with water and alcohol. Analytical data of the materials correspond to $R.P_2O_5$ when R is hexadecene, octene and dodecene, and to $R.P_2O_4$ when R is *cyclo*hexene, styrene and ethylene. With *cyclo*hexene the polymeric structure is made up of the units:



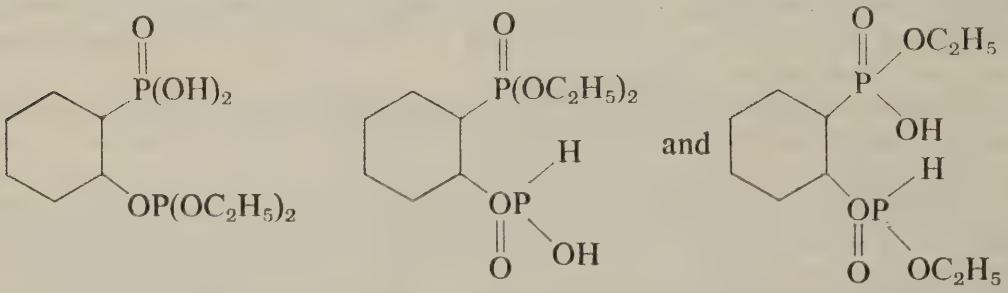
Oxidative hydrolysis of this material with 45% nitric acid proceeds according to the following scheme:



Hydrolysis with water proceeds as follows:



Aqueous alcohol forms esterified products, of which the most likely structures appear to be:



## Silicon, Sulphur, Arsenic, Selenium and Tellurium

Vapour pressure studies indicate the existence of a silicon phosphide, SiP, but no compound $Si_3P_4$, analogous to thorium phosphide, exists.[138] The monophosphide is formed by reaction of the elements at temperatures above 1100°C.[139]

A disilicon phosphide, $Si_2P$, has been prepared as a blue-black amorphous solid by heating phosphine and silane at 450°C. and 200 mm. total pressure. It decomposes at 600°C. into silicon and silicon monophosphide.[140] Further details of these phosphides are given in Sections VII and VIII.

Sulphur and white phosphorus form solid solutions on mixing the elements at temperatures below 100°C. Above this temperature a vigorous exothermic reaction occurs with the formation of $P_4S_3$, $P_4S_5$, $P_4S_7$ and $P_4S_{10}$ (ref. 66, p. 290). In addition less well-defined compounds of composition $P_4S_2$,[320] PS[321] and $PS_{5-7}$[322] have been described, as well as a phase of variable composition $P_4S_{6-7}$, which appears to be a defect form of the heptasulphide.[323] These products are described in detail in Section XI.

The band spectrum of the diatomic molecule PS has been studied.[73, 141] A polymeric form, $(PS)_n$, which is a yellow powder insoluble in common organic solvents, has been described.[142] The heat capacity of the PS molecule has been calculated from spectroscopic constants with the results shown in Table XVIII.[143]

Four phosphorus oxysulphides, $P_4O_6S_4$,[144-5] $P_4O_4S_6$,[146] $P_4O_4S_3$[147] and $P_6O_{10}S_5$,[145] have been described. The best-defined of these compounds is $P_4O_6S_4$.[144] These materials are described in Section XII.

Phosphorus and arsenic react to form a monophosphide, AsP, a black substance similar to graphite. The existence of this is shown by *X*-ray and thermal analysis of the phosphorus–arsenic system.[148]

Mixtures of selenium and phosphorus combine on heating to form the selenides $P_2Se_3$ and $P_2Se_5$ according to the proportion of the elements used. In carbon disulphide solution in the presence of naphthalene $P_4Se_3$, a yellow or orange product, is formed. It melts at 242°C.[149] The same material is produced slowly when selenium is dissolved in molten white phosphorus. Solid solutions are formed at temperatures below 50°C. and at 130°C. a slow reaction begins.[150] This selenide is also formed in about 30% yield by heating selenium and phosphorus in tetralin solution at 215° to

220°C.[151] The density is 1·31 and the structure is similar to that of $P_4S_3$ except that the unit cell is about twice as large.[152] In moist air it forms hydrogen selenide and aqueous sodium hydroxide gives phosphine and sodium selenide. Iodine in carbon disulphide produces $P_4Se_3I_2$, m.p. 154° to 155°C., which reacts explosively with nitric acid.[153]

*Table XVIII.—Calculated Heat Capacity of the* PS *Molecule*[143]

| Temp. °K. | $C_p$ g.-cal./mole | Temp. °K. | $C_p$ g.-cal./mole | Temp. °K. | $C_p$ g.-cal./mole |
|---|---|---|---|---|---|
| 100 | 6·963 | 1200 | 8·889 | 3200 | 9·116 |
| 200 | 7·246 | 1400 | 8·933 | 3400 | 9·129 |
| 300 | 7·740 | 1600 | 8·967 | 3600 | 9·143 |
| 400 | 8·118 | 1800 | 8·993 | 3800 | 9·155 |
| 500 | 8·368 | 2000 | 9·016 | 4000 | 9·169 |
| 600 | 8·531 | 2200 | 9·036 | 4200 | 9·183 |
| 700 | 8·643 | 2400 | 9·054 | 4400 | 9·195 |
| 800 | 8·722 | 2600 | 9·070 | 4600 | 9·207 |
| 900 | 8·780 | 2800 | 9·086 | 4800 | 9·221 |
| 1000 | 8·825 | 3000 | 9·102 | 5000 | 9·233 |

Powdered tellurium and white phosphorus form a tritelluride, $P_2Te_3$, by heating in a sealed tube at 320°C., but red phosphorus does not react. It is a black solid, *d* 4·13, which in moist air slowly evolves phosphine. In air it ignites at 330°C. forming phosphorus pentoxide and tellurium, but in a sealed tube tellurium and phosphorus result. Iodine in carbon disulphide gives $P_2Te_3I_2$, a black material which is also formed by reaction of carbon disulphide solutions of white phosphorus and tellurium iodide, $TeI_2$.[154]

No binary compounds of phosphorus and antimony exist according to phase diagram studies.[155]

### Halogens

The diatomic phosphorus halides PCl, PBr and PI are unstable under normal conditions but have been identified in band spectra.[156] Direct combination of phosphorus with the halogens is spontaneous and exothermic. Reactions with white phosphorus can be explosive, but those with red phosphorus are easier to control. Iodine does not form a pentaiodide, giving only $PI_3$ and $P_2I_4$. The other halogens form both penta- and trihalides but no dihalide, except for chlorine, though $P_2F_4$ has been prepared by an indirect procedure.[324] The preparation of $PF_3$,[157–8] $PCl_3$[159] and $PBr_3$[60] have been described in detail. The reaction between phosphorus and iodine in carbon tetrachloride solution to form $P_2I_4$ involves a chain mechanism which can be represented by the following stages:

(1) $P_4+I_2 = P_4I_2$
(2) $P_4I_2 = P_2I_2+P_2$
(3) $P_2I_2+P_4 = P_4I_2+P_2$
(4) $P_2+I_2 = P_2I_2$
(5) $P_2I_2+I_2 = P_2I_4$
(6) $2P_2I_2 = P_2I_4+P_2$

On the assumption (which is not completely justified by the data) that the concentrations of $P_2$, $P_2I_2$ and $P_4I_2$ reach a steady state during the reaction, the rate equation is:

$$\frac{-\mathrm{d}[I_2]}{\mathrm{d}t} = 4[I_2]\left(\frac{a[P_4][I_2]}{[I_2]-b[P_4]}\right) + c\left(\frac{a[P_4][I_2]}{[I_2]-b[P_4]}\right)^2$$

where $a=k_1$, $b=2k_3/k_5$ and $c=4k_6/k_5^2$; and $k_1$, $k_3$, $k_5$ and $k_6$ are the rate constants for the equations given above, in millimoles/litre/min. For a reaction carried out in the dark at 15°C. in an atmosphere of carbon dioxide the values of *a*, *b* and *c* are 100, 0·04 and 0·06, respectively.[161] Later workers have criticized the assumptions on which these experiments were based.[325]

Phosphorus forms a number of higher or poly-halides containing seven or more halogen atoms per atom of phosphorus. Several mixed halides, which are not simply mixtures, have been obtained by prolonged heating of the pure trihalides. The formulæ of these are $PXY_2$ and $PX_2Y$, where X and Y are halogen atoms. Raman spectra of heated mixtures of the trihalides show the existence of PFClBr. The oxyhalides $POX_3$ and thiohalides $PSX_3$ are well known and a number of more complex compounds of this type, e.g. $P_2O_3Cl_4$, $P_2S_3Br_4$, has been obtained. Mixed halides such as $POX_2Y$, $POXY_2$, $PSX_2Y$ and $PSXY_2$ have been described. These, and the simpler phosphorus halides, are discussed in more detail in Sections XIII to XVII.

Phosphorus pentahalides react with ammonia or ammonium halides to form the phosphonitrilic halides $(PNX_2)_n$, which are described in Section XVIII.

Some halogen-containing compounds of phosphorus are listed in Table XIX.

*Table XIX.—Some Halogen-containing Compounds of Phosphorus*

| Simple halides | Mixed halides | Oxy- and thio-halides | Complex halides | Higher halides | Mixed oxy- and thio-halides | Nitrogen–halogen compounds |
|---|---|---|---|---|---|---|
| $PF_5$ | $PF_4Cl$ | $POF_3$ | $PO_2F$ | $PCl_6I$ | $POF_2Cl$ | $(PNF_2)_3$ |
| $PCl_5$ | $PF_3Cl_2$ | $POCl_3$ | $PO_2Cl$ | $PCl_5Br_{10}$ | $POF_2Br$ | $(PNF_2)_4$ |
| $PBr_5$ | $PF_3Br_2$ | $POBr_3$ | $PO_2I_2$ | $PCl_5BrI$ | $POFCl_2$ | $(PNCl_2)_n$ |
| $PF_3$ | $PF_3I_2$ | $PSF_3$ | $P_2OF_4$ | $PCl_3Br_4$ | $POFBr_2$ | $(PNBr_2)_n$ |
| $PCl_3$ | $PF_2Cl_3$ | $PSCl_3$ | $P_2O_2Cl_5$ | $PCl_3Br_8$ | $POFClBr$ | $(PNFCl)_4$ |
| $PBr_3$ | $PF_2Br_3$ | $PSBr_3$ | $P_2O_3F_4$ | $PCl_3Br_{18}$ | $POCl_2Br$ | $P_3N_3Cl_2F_4$ |
| $PI_3$ | $PFCl_4$ | | $P_2O_3Cl_4$ | $PCl_2Br_7$ | $POClBr_2$ | $P_3N_3Cl_4F_2$ |
| $P_2F_4$ | $PFBr_4$ | | $P_2OS_2Cl_4$ | $PClBr_5I$ | $PSF_2Br$ | |
| $P_2Cl_4$ | $PCl_4Br$ | | $P_3O_8I_6$ | $PBr_{17}$ | $PSFBr_2$ | |
| $P_2I_4$ | $PCl_3Br_2$ | | $P_7O_{15}Cl_5$ | $PBr_7$ | $P_2O_3Cl_2F_2$ | |
| $PCl$ | $PCl_2Br_3$ | | $PSI$ | $PBr_6I$ | | |
| $PBr$ | $PClBr_4$ | | $PS_2Cl_5$ | | | |
| $PI$ | $PF_2Cl$ | | $PS_5Cl_2$ | | | |
| | $PF_2Br$ | | $PS_{24}I_3$ | | | |
| | $PF_2I$ | | $P_2SBr_6$ | | | |
| | $PFCl_2$ | | $P_2SI_4$ | | | |
| | $PFBr_2$ | | $P_2SI_2$ | | | |
| | $PFClBr$ | | $P_2S_3Br_4$ | | | |
| | $PCl_2Br$ | | $P_4S_3I_2$ | | | |
| | $PClBr_2$ | | | | | |
| | $PBr_2I$ | | | | | |
| | $PBrI_2$ | | | | | |

In addition to the above there are numerous other phosphorus compounds which contain halogens, including phosphonium halides $PH_4X$, chlorinated phosphines, fluorinated phosphines and phosphoranes, addition compounds of phosphorus trihalides and pentahalides with halides of other elements and organic phosphorus halogen compounds. For details of these reference should be made to Sections XIII to XVIII and XXXI to XXXIII, Mellor, VIII, 993–1041, and Van Wazer (ref. 66).

Compounds such as $P(CN)_3$, $P(NCO)_3$ and $P(NCS)_3$, which are similar to the phosphorus trihalides, also $PO(NCO)_3$ and $PO(NCS)_3$, similar to the oxyhalides, and $PS(NCO)_3$, resembling the thiohalides, have been described.[162–5]

The viscosities of phosphorus vapour and several diatomic phosphorus compounds have been estimated[143] for gases in the ground state and 1 atm. pressure, using the expression:

$$\eta = \frac{26{\cdot}693\sqrt{MT}}{\sigma^2\Omega}$$

where $\eta$ is the viscosity in micropoises, $M$ is molecular weight, $T$ is absolute temperature, and $\sigma$ is the collision diameter in Ångström units. $\Omega$ is the reduced collision integral, which is a function of the reduced temperature $kT/\epsilon$, where $k$ is Boltzmann's constant and $\epsilon$ ergs is the maximum energy of attraction between colliding molecules. Values of $\Omega$ have been tabulated.[166] Representative values of $\eta$ are given in Table XX.

*Table XX.—Calculated Viscosity of Molecules of Phosphorus and Some Phosphorus Compounds*[143]

| Temp. °K. | Viscosity in micropoises | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | P | $P_2$ | $P_4$ | PC | PN | PO | PS | PF |
| 100 | — | — | — | 37·8 | 40·6 | 41·2 | — | 43·2 |
| 200 | 45·0 | 45·1 | 49·6 | 75·5 | 81·4 | 81·0 | 46·9 | 84·6 |
| 300 | 64·8 | 64·9 | 71·0 | 112·8 | 121·2 | 121·8 | 66·9 | 127·4 |
| 400 | 85·9 | 86·1 | 93·7 | 147·1 | 157·4 | 160·5 | 87·9 | 168·1 |
| 500 | 107·7 | 108·0 | 117·3 | 178·0 | 190·0 | 196·0 | 110·0 | 205·6 |
| 600 | 129·7 | 130·1 | 141·3 | 206·4 | 219·9 | 228·6 | 132·4 | 240·0 |
| 700 | 151·3 | 151·7 | 165·1 | 232·7 | 247·5 | 258·8 | 154·9 | 272·0 |
| 800 | 172·5 | 173·0 | 188·5 | 257·3 | 273·4 | 287·2 | 176·9 | 302·0 |
| 900 | 193·2 | 193·8 | 211·5 | 280·4 | 297·8 | 313·9 | 198·7 | 330·4 |
| 1000 | 213·3 | 213·8 | 233·9 | 302·5 | 321·0 | 359·3 | 220·0 | 357·2 |
| 1200 | 251·2 | 251·9 | 276·7 | 343·5 | 364·1 | 386·8 | 260·7 | 407·5 |
| 1400 | 286·5 | 287·3 | 316·6 | 381·6 | 404·4 | 430·6 | 298·9 | 453·8 |
| 1600 | 319·7 | 320·6 | 354·2 | 417·7 | 442·5 | 471·8 | 334·9 | 497·3 |
| 1800 | 351·1 | 352·1 | 389·8 | 451·9 | 478·5 | 511·0 | 368·9 | 538·7 |
| 2000 | 381·0 | 382·0 | 423·6 | 484·4 | 512·8 | 548·4 | 401·3 | 578·3 |
| 2500 | 450·0 | 451·2 | 502·0 | 559·9 | 592·3 | 635·3 | 476·4 | 670·2 |
| 3000 | 512·8 | 514·2 | 573·4 | 629·4 | 665·9 | 714·6 | 544·7 | 754·1 |
| 3500 | 570·7 | 572·3 | 639·1 | 696·0 | 737·1 | 788·9 | 607·8 | 832·4 |
| 4000 | 625·3 | 627·0 | 700·7 | 760·0 | 804·4 | 860·6 | 666·8 | 907·7 |
| 4500 | 677·2 | 679·0 | 759·2 | 820·7 | 868·5 | 930·3 | 722·7 | 981·3 |
| 5000 | 726·7 | 728·7 | 815·2 | 878·8 | 930·0 | 996·5 | 776·2 | 1051·3 |

*Table XXI.—Thermal Conductivity of Phosphorus Compounds*[143]

| Temp. °K. | Total thermal conductivity $\lambda \times 10^6$ g.-cal./cm. sec. °K. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | P | $P_2$ | $P_4$ | PC | PN | PO | PS | PF |
| 100 | — | — | — | 8·9 | 9·1 | 8·8 | — | 8·7 |
| 200 | 10·8 | 7·6 | 7·4 | 17·8 | 18·3 | 17·4 | 7·8 | 17·3 |
| 300 | 15·6 | 11·5 | 12·7 | 27·1 | 27·7 | 26·8 | 11·8 | 27·4 |
| 400 | 20·7 | 16·0 | 18·1 | 36·7 | 37·1 | 36·7 | 16·2 | 37·8 |
| 500 | 25·9 | 20·7 | 23·7 | 46·0 | 46·4 | 46·4 | 20·8 | 47·9 |
| 600 | 31·2 | 25·4 | 29·2 | 54·9 | 55·3 | 55·7 | 25·5 | 57·3 |
| 700 | 36·4 | 30·0 | 34·7 | 63·3 | 63·7 | 64·5 | 30·2 | 66·1 |
| 800 | 41·5 | 34·5 | 39·9 | 71·2 | 71·6 | 72·8 | 34·8 | 74·4 |
| 900 | 46·5 | 38·9 | 45·1 | 78·6 | 79·1 | 80·6 | 39·3 | 82·2 |
| 1000 | 51·3 | 43·2 | 50·1 | 85·7 | 86·2 | 88·0 | 43·8 | 89·5 |
| 1200 | 60·4 | 51·2 | 59·7 | 98·7 | 99·4 | 101·7 | 52·2 | 103·3 |
| 1400 | 69·0 | 58·7 | 68·6 | 110·7 | 111·6 | 114·3 | 60·2 | 116·0 |
| 1600 | 77·2 | 65·8 | 76·9 | 122·0 | 123·0 | 126·1 | 67·6 | 128·0 |
| 1800 | 85·2 | 72·4 | 84·8 | 132·7 | 133·8 | 137·3 | 74·7 | 139·4 |
| 2000 | 93·2 | 78·8 | 92·3 | 142·8 | 144·0 | 147·9 | 81·5 | 150·3 |
| 2500 | 114·2 | 93·5 | 109·5 | 166·3 | 167·6 | 172·6 | 40·8 | 176·0 |
| 3000 | 137·6 | 106·9 | 125·2 | 187·9 | 189·4 | 195·2 | 47·1 | 199·7 |
| 3500 | 162·7 | 119·4 | 139·7 | 208·7 | 210·6 | 220·5 | 53·0 | 222·3 |
| 4000 | 188·4 | 131·3 | 153·2 | 228·8 | 230·6 | 236·9 | 58·7 | 244·3 |
| 4500 | 213·4 | 142·6 | 166·1 | 247·9 | 249·8 | 256·9 | 64·1 | 266·1 |
| 5000 | 236·5 | 153·9 | 178·3 | 266·3 | 268·3 | 276·1 | 69·3 | 287·2 |

Thermal conductivities have been estimated[143] in a similar way from the expression:

$$\lambda = \lambda_1 + \lambda_2 = \frac{R}{M}\left[\frac{15}{4} + 1{\cdot}32\left(\frac{C_p}{R} - \frac{5}{2}\right)\right]\eta$$

where $\lambda$ is the total thermal conductivity in g.-cal./cm. sec. °K., $\lambda_1$ and $\lambda_2$ are the coefficients for translational and internal conductivity, respectively. The viscosity $\eta$ is in poises. Selected conductivity values are given in Table XXI. The translational conductivity was calculated from the expression:

$$\lambda_1 = \frac{15R}{4M}\eta$$

## THE REACTIONS OF PHOSPHORUS WITH METALLIC ELEMENTS

Phosphorus under suitable conditions reacts with all metallic elements except bismuth, mercury and lead. The products of these reactions are phosphides, the preparation and properties of which are more fully described in Section VII.

Some metals, e.g. calcium, magnesium and beryllium, form only one phosphide, but in most cases more than one phosphide is known. The resulting compounds may be simple molecules which are readily volatilized, complex polymeric materials, or compounds having properties rather similar to those of hard metals such as iron. The binary compounds of phosphorus with metals of Group IA and Group IIA of the Periodic Table are described as being salt-like in properties, but there does not seem to be conclusive evidence in support of this. Elements of Groups IIIA, IVA and VA generally give covalently bonded molecules. The transition metal phosphides usually have a high melting point, are fairly resistant to chemical attack, and conduct heat and electricity to some extent.

Several general methods can be used for causing phosphorus to react with the metallic elements. The simplest is to heat the metal with red or white phosphorus, or with phosphorus vapour, in a non-oxidizing atmosphere. With some elements phosphorus can be added to a bath of the molten metal. The more volatile and easily oxidized elements, e.g. sodium, are often covered with an inert liquid such as paraffin during reaction with phosphorus. Thermally unstable phosphides have been made by heating the metal under pressure with excess of phosphorus in a closed system at temperatures up to 1000°C. At the end of the reaction the excess of phosphorus is condensed in another part of the apparatus.[167–8] When phosphorus reacts in more than one proportion with an element, advantage can be taken of the fact that some of the products may be thermally more unstable than others.[169]

The alkali metals react with phosphorus on heating in a vacuum at temperatures up to 450°C. to yield phosphides of the formula $M_2P_5$, where M is the alkali metal.[170] Liquid white phosphorus in an inert atmosphere reacts with alkali metals to give materials corresponding to $M_3P$. The existence of these as pure compounds has been doubted.[66] Lithium and liquid white phosphorus react in liquid ammonia, and on removing excess of phosphorus from the product by heating in a vacuum at 280°C. a product with the composition LiP is obtained. This compound is also formed by heating lithium in phosphorus vapour at temperatures below 400°C. It reacts with more lithium to give $Li_3P$.[22] Liquid ammonia reactions also form $Li_2P$, $Na_2P$ and $K_3P_2$.[171] The properties of these compounds suggest that they are dimeric, i.e. $Li_4P_2$, $Na_4P_2$ and $K_6P_4$.[172] For other alkali-metal phosphides, e.g. $Li_2PH$, $NaPH_2$, which are not formed by direct combination with phosphorus, Section VII should be consulted.

Phosphorus reacts with the lithium–aluminium alloy $Li_3Al$ on heating to form a mixed phosphide $Li_3AlP_2$. The same product results when phosphorus is heated with a mixture of aluminium metal and $Li_3P$.[173] The reaction of phosphorus, $Li_3P$ and a metal in a bomb at 500° to 1000°C. has been used to prepare $Li_3GaP_2$, $Li_5GeP_3$, $Li_5SiP_3$ and $Li_5TiP_3$.[174]

Direct combination of phosphorus with copper, silver and gold occurs less readily than with the alkali metals. At high temperatures and pressures, copper and phosphorus vapour form $CuP_2$. The latter decomposes according to the equation:

$$12CuP_2 = 4Cu_3P + 5P_4$$

The partial pressure of phosphorus vapour ($P_4$) for this reaction is given by[175, 168]:

$$\log_{10} p_{mm.} = -\frac{11{,}370}{T} + 13{\cdot}827$$

The phosphide $Cu_3P$ has also been made by heating the theoretical proportions of copper and red phosphorus for 20 hr. at 640°C. in a vacuum and then raising the temperature to 1000°C. for 5 hr.[175]

At temperatures above 500°C. phosphorus vapour reacts slowly with finely-divided silver and gold to form $AgP_3$, $AgP_2$ and $Au_2P_3$. These materials decompose when heated, according to the following equations[167–8]:

$$\begin{aligned} 4AgP_3 &= 4AgP_2 + P_4 \\ 2AgP_2 &= 2Ag + P_4 \\ 12Au_2P_3 &= 8Au_3P + 7P_4 \\ 4Au_3P &= 12Au + P_4 \end{aligned}$$

The partial pressures of $P_4$ are given by:

$AgP_3$ $$\log_{10} p_{mm.} = -\frac{7766}{T} + 12{\cdot}74$$

$AgP_2$ $$\log_{10} p_{mm.} = -\frac{7180}{T} + 11{\cdot}60$$

$Au_2P_3$ $$\log_{10} p_{mm.} = -\frac{9124}{T} + 12{\cdot}21$$

Red and white phosphorus react with beryllium, magnesium and the alkaline earth metals in the manner already described (Mellor, VIII, 833) to give phosphides of the type $M_3P_2$. Red phosphorus and barium, when heated at 400° to 450°C., are reported to form a crystalline material having the empirical formula $BaP_3$. At 750°C. this is converted into $BaP_2$ and at higher temperatures the normal phosphide $Ba_3P_2$ is obtained.[176]

Liquid ammonia solutions of the alkaline earth metals react with phosphorus to give products of somewhat uncertain composition, e.g. $Ca(PH_2)_2,6NH_3$.[177]

Zinc or cadmium reacts with red phosphorus when heated in a sealed tube to form the diphosphides $MP_2$. These melt at about 700°C. and sublime in an atmosphere of phosphorus vapour.[178] In a vacuum at 500°C. they decompose to give the lower phosphides $M_3P_2$.[179] Heating red phosphorus in a sealed tube with cadmium–lead alloys for several days at 565°C. forms $CdP_4$.[180] Mercury does not react directly with phosphorus.

Several aluminium phosphides have been reported (Mellor, VIII, 846), but more recent work indicates that on heating aluminium in a stream of phosphorus vapour and hydrogen only a monophosphide, AlP, is formed.[181] Phosphorus reacts slowly with gallium or indium in a vacuum at 700°C. forming GaP and InP.[182–3]

In the earlier literature (Mellor, VIII, 846) thallium phosphide was not thought to exist. However, a later phase study suggested that red phosphorus and thallium form $TlP_3$ at about 400°C.[184] High pressures are necessary for its formation. Theoretical amounts of thallium and white phosphorus form $Tl_3P$ in a sealed tube at 400°C.[185]

Germanium and tin react when heated with excess of phosphorus in an evacuated sealed tube at above 400°C. and below 350°C., respectively. The formula of the germanium phosphide is GeP[186] and that of the tin compound is $SnP_3$. The latter loses phosphorus at above 350°C. in a vacuum to give $Sn_4P_3$ (Mellor, VIII, 848).

More recently[187] a tin phosphide, SnP, has been obtained by heating a 1:3 atom weight ratio of tin and red phosphorus at 700°C. in a vacuum ($10^{-6}$ mm. Hg). The product is then cooled at about 40°C./hr. Lead does not appear to react directly with phosphorus to form a definite compound, although $PbP_2$ has been reported (Mellor, VIII, 849). Alloys of lead with zinc, cadmium and mercury form ternary compounds $MPbP_{14}$ when heated with phosphorus at 500° to 600°C. for up to ten days.[188]

Lanthanum reacts violently with phosphorus at 400° to 500°C. in a sealed tube to form LaP.[189] Scandium and yttrium phosphides, ScP and YP, have been prepared by heating the element with red phosphorus in an evacuated silica tube for 30 hr. at 1000°C.[190] A hafnium phosphide, HfP, has been reported,[191] as has a diphosphide, $HfP_2$.[326]

Zirconium, vanadium, niobium and tantalum all react with excess of red phosphorus on heating in evacuated sealed tubes for periods up to 30 days at temperatures between 550° and 1100°C.[192] They all form diphosphides, $MP_2$, which decompose to form monophosphides:

$$4MP_2 = 4MP + P_4$$

The partial pressure of phosphorus vapour over a mixture of the two phosphides, as derived from experimental data, is given for three of the metals by the following equations:

$ZrP_2$[193] $$\log_{10} p_{\text{mm.}} = 12{\cdot}05 - \frac{10{,}800}{T}$$

$VP_2$[169] $$\log_{10} p_{\text{mm.}} = 15{\cdot}37 - \frac{12{,}400}{T}$$

$TaP_2$[194] $$\log_{10} p_{\text{mm.}} = 14{\cdot}48 - \frac{13{,}200}{T}$$

A compound which may be $Zr_3P$ has been obtained by controlled heating of zirconium and phosphorus in a sealed tube for varying successive periods at 500° to 600°C., 800°C. and 900° to 1000°C., followed by cooling at a rate of 100°C./hr.[193]

Titanium diphosphide, $TiP_2$, does not appear to be obtained easily by direct synthesis.[192] The product formed by heating the elements in a sealed tube at 600° to 800°C. is the monophosphide TiP.[195] Phosphorus and excess of titanium form $Ti_3P$ when heated for 48 hr. at 800°C. in an evacuated silica tube.[196–8]

Niobium, like titanium, does not give a diphosphide by direct reaction with phosphorus. However, by heating niobium with excess of red phosphorus at 750°C. under pressure, the compound $NbP_{2\cdot4}$ is obtained. This decomposes to the diphosphide when heated at 430°C. in a vacuum.[199]

When red phosphorus is heated in a closed system with chromium, molybdenum or rhenium, diphosphides are formed.[192, 200–17] These reactions are generally slow and may require up to 100 hr. for completion. Chromium reacts in 75 hr. at 600° to 750°C.,[200] and the temperatures for molybdenum and tungsten are 550° to 1000°C. and 700° to 970°C., respectively.[200] Rhenium reacts only above 800°C., forming mainly the triphosphide $ReP_3$. Further heating at atmospheric pressure gives the diphosphide.[201] Manganese does not form a diphosphide.[202] It reacts with red phosphorus at 300° to 350°C., but temperatures of 1000°C. are necessary to form a homogeneous product.[202–3] The main product is the triphosphide, $MnP_3$. A monophosphide has been made directly by dropping pellets of red phosphorus into molten manganese in a sealed tube in an atmosphere of argon. The product is then heated with more red phosphorus in an evacuated silica tube at 900° to 1150°C.[204]

A tungsten monophosphide has been obtained by fused salt electrolysis,[205] by thermal decomposition of $W_3P$[205] or $WP_2$[200] and by direct synthesis.[200] At 950° to 1300°K. it decomposes into tungsten and mainly diatomic phosphorus. The $P_2$ decomposition pressure is given by the equation[205]:

$$\log_{10} p_{\text{atm.}}[P_2] = 8{\cdot}501 - \frac{16{,}534}{T}$$

Chromium, molybdenum and tungsten diphosphides decompose according to the equation:

$$4MP_2 = 4MP + P_4$$

The partial vapour pressures of $P_4$ over these phosphides are[200]:

$CrP_2$ $\qquad \log_{10} p_{\text{mm.}} = 11{\cdot}582 - \dfrac{8540}{T}$

$MoP_2$ $\qquad \log_{10} p_{\text{mm.}} = 12{\cdot}425 - \dfrac{12{,}000}{T}$

$WP_2$ $\qquad \log_{10} p_{\text{mm.}} = 13{\cdot}090 - \dfrac{13{,}800}{T}$

For manganese triphosphide obtained from its elements at 610° to 720°C. under pressure, the decomposition equation is[203]:

$$2MnP_3 = 2MnP + P_4$$

The $P_4$ partial pressure in this decomposition is given by:

$$\log_{10} p_{\text{mm.}} = 14{\cdot}948 - \frac{11{,}856}{T}$$

Heating manganese and red phosphorus in an evacuated sealed tube at 650°C. is reported to give $Mn_2P$ and $Mn_4P$.[204]

Rhenium triphosphide decomposes in the following stages to form lower phosphides[201]:

$$\begin{aligned} 4ReP_3 &= 4ReP_2 + P_4 \\ 4ReP_2 &= 4ReP + P_4 \\ 4ReP &= 2Re_2P + P_2 \end{aligned}$$

The vapour pressure equations for these reactions are:

$ReP_3$ $\qquad \log_{10} p_{\text{mm.}} = 16{\cdot}77 - \dfrac{17{,}060}{T}$

$ReP_2$ $\qquad \log_{10} p_{\text{mm.}} = 13{\cdot}37 - \dfrac{14{,}220}{T}$

$ReP$ $\qquad \log_{10} p_{\text{mm.}} = 10{\cdot}90 - \dfrac{13{,}780}{T}$

Red phosphorus and iron react when heated for periods up to 24 hr. at 600° to 1000°C. and 1–2 atm. pressure. The compounds $FeP_2$ and $FeP$ are formed, and these decompose when heated at atmospheric pressure, according to the equations[207]:

$$\begin{aligned} 4FeP_2 &= 4FeP + P_4 \\ 4FeP &= 2Fe_2P + P_2 \end{aligned}$$

The partial pressures of $P_4$ and $P_2$, respectively, for these reactions are given by[210]:

$FeP_2$ $\qquad \log_{10} p_{\text{mm.}} = 14{\cdot}469 - \dfrac{14{,}650}{T}$

$FeP$ $\qquad \log_{10} p_{\text{mm.}} = 13{\cdot}230 - \dfrac{17{,}580}{T}$

According to more recent data for the reactions[211]:

$$\begin{aligned} 2FeP_2 &= 2FeP + P_2 \\ 4FeP &= 2Fe_2P + P_2 \\ 6Fe_2P &= 4Fe_3P + P_2 \end{aligned}$$

the equations for the partial pressure of $P_2$ are:

$$\mathrm{FeP_2} \qquad \log_{10} p_{\mathrm{mm.}} = 13{\cdot}381 - \frac{15{,}400}{T}$$

$$\mathrm{FeP} \qquad \log_{10} p_{\mathrm{mm.}} = 14{\cdot}001 - \frac{18{,}700}{T}$$

$$\mathrm{Fe_2P} \qquad \log_{10} p_{\mathrm{mm.}} = 14{\cdot}161 - \frac{24{,}040}{T}$$

Cobalt and red phosphorus combine to form $CoP_3$, CoP and $Co_2P$ on heating for up to 200 hr. in a closed system at 600° to 650°C.[212–3] The triphosphide decomposes on heating according to the equation:

$$2\mathrm{CoP_3} = 2\mathrm{CoP} + \mathrm{P_4}$$

for which the $P_4$ partial pressure is given by[212]:

$$\log_{10} p_{\mathrm{mm.}} = 14{\cdot}397 - \frac{15{,}650}{T}$$

The compound $Co_2P$ has been obtained by heating red phosphorus with molten cobalt at reduced pressure in a closed system under argon. The product is then heated with more cobalt in a vacuum.[213] A similar technique was used for CoP, the product (largely $Co_2P$) then being heated with red phosphorus in evacuated sealed tubes at 900° to 1150°C.[212]

The phosphides $NiP_3$, $NiP_2$ and $Ni_6P_5$ are obtained on heating nickel and red phosphorus in a closed system for up to 100 hr. at 600° to 700°C.[214] The decomposition and $P_4$ partial pressure equations are:

$$\begin{aligned} 4\mathrm{NiP_3} &= 4\mathrm{NiP_2} + \mathrm{P_4} \\ \tfrac{24}{7}\mathrm{NiP_2} &= \tfrac{4}{7}\mathrm{Ni_6P_5} + \mathrm{P_4} \\ 2\mathrm{Ni_6P_5} &= 6\mathrm{Ni_2P} + \mathrm{P_4} \end{aligned}$$

$$\mathrm{NiP_3} \qquad \log_{10} p_{\mathrm{mm.}} = 12{\cdot}870 - \frac{9{,}350}{T}$$

$$\mathrm{NiP_2} \qquad \log_{10} p_{\mathrm{mm.}} = 14{\cdot}320 - \frac{12{,}450}{T}$$

$$\mathrm{Ni_6P_5} \qquad \log_{10} p_{\mathrm{mm.}} = 14{\cdot}965 - \frac{13{,}750}{T}$$

The cobalt and nickel phosphides are somewhat more easily obtained by heating red phosphorus at 600°C. with alloys of tin containing 5% of cobalt or nickel. The tin triphosphide, $SnP_3$, which is also formed, is then converted to $Sn_4P_3$ by heating in a vacuum at 350°C. and the $Sn_4P_3$ is removed by dissolving it in hydrochloric acid.[214–5]

Heating ruthenium and red phosphorus in evacuated sealed tubes at 500° to 1100°C. gives the phosphides $RuP_2$, RuP and $Ru_2P$.[216] Excess of phosphorus at 650° to 680°C. for 34–48 hr. forms $RuP_2$ and at 800° to 900°C. RuP results.[217–8] Excess of ruthenium gives $Ru_2P$.[213]

A diphosphide, $RhP_2$, is obtained when rhodium and red phosphorus are heated under pressure in a sealed tube at 800° to 1100°C.[218–20] A triphosphide, $RhP_3$, and the compound $Rh_5P_4$ have been obtained in a similar manner,[218] although the latter is more probably identical with $Rh_4P_3$.[220] Rhodium triphosphide decomposes at about 1000°C. according to the equation:

$$4\mathrm{RhP_3} = 4\mathrm{RhP_2} + \mathrm{P_4}$$

The $P_4$ partial pressure equation for this decomposition is[219]:

$$\log_{10} p_{\text{mm.}} = 11{\cdot}713 - \frac{12{,}850}{T}$$

At 900° to 1100°C. in evacuated sealed tubes the phosphides $Rh_4P_3$[220-1] and $Rh_2P$[220, 216] are formed from the elements.

The products obtained when red phosphorus and palladium are heated in various proportions in evacuated sealed tubes at 500° to 1100°C. have been shown to be $PdP_3$,[216, 220] $PdP_2$[218] and $Pd_5P_2$.[222] At 700°C. $Pd_3P$ is also formed[222-3]; the composition of this material appears to vary slightly[224, 222] but its existence has been confirmed by *X*-ray methods.[225] The compound $Pd_7P_3$ has been prepared by heating palladium and red phosphorus in an evacuated silica tube at 1200°C. and rapidly quenching from 750°C., and may be identical with $Pd_5P_2$ mentioned above.[226]

Osmium, iridium and platinum form diphosphides when heated with red phosphorus at temperatures above 700°C.[218] The osmium compound, $OsP_2$, is prepared by heating the metal with red phosphorus at 1000°C. and then condensing the excess of phosphorus at 500°C. Osmium also reacts with phosphorus vapour at 1190°C.[217]

Iridium and excess of red phosphorus form $IrP_2$ on heating for 280 hr. at 650°C. This product is also formed by heating the mixture for 96 hr. at 820°C. and then distilling off the excess of phosphorus at 427°C.[218] At 1000°C. in a vacuum the triphosphide $IrP_3$ is obtained.[227] Iridium diphosphide decomposes in a vacuum at 1150°C. to form $Ir_2P$, which is also obtained by heating red phosphorus with excess of iridium for 146 hr. at 990°C.

Platinum reacts with excess of red phosphorus when heated at 800° to 1100°C. in an evacuated tube to form $PtP_2$.[216, 218] It is also formed on heating the elements under pressure for 10 hr. at 600°C.[228] Phosphorus and excess of platinum heated for 2 hr. at 500°C. and then for one day at 750°C. form $Pt_{20}P_7$. A eutectic (m.p. 588°C.) of this compound and platinum is the cause of the embrittlement and corrosion of platinum crucibles by small amounts of phosphorus.[229]

The more usual compounds formed when the actinide elements are heated under pressure with red phosphorus are the phosphides MP and $M_3P_4$. Excess of phosphorus and thorium form $Th_3P_4$ at 650° to 700°C.[230-1] The monophosphide ThP also appears to exist.[232]

Uranium and excess of red phosphorus, under pressure at 800° to 900°C., form $U_3P_4$, $UP_2$ and UP.[233, 231] The diphosphide is also obtained by heating the elements for two days at 550°C.[234] The monophosphide forms when $U_3P_4$ is decomposed by heating in a vacuum at 1400°C.[235] On further heating at 1500° to 2000°C. under ordinary pressure, the monophosphide decomposes according to the equations:

$$\begin{aligned} UP(s) &= U(g)+\tfrac{1}{2}P_2(g) \\ UP(g) &= U(g)+P(g) \end{aligned}$$

The respective heats of reaction ($\Delta H^\circ$) at 1750°C. are $184{\cdot}4 \pm 3{\cdot}1$ kcal./mole and $251{\cdot}6 \pm 4{\cdot}9$ kcal./mole. The partial vapour pressure equations are[236]:

$$\log_{10} p_{\text{atm.}}\,[P] = 6{\cdot}41 - \frac{26{,}211}{T}$$

$$\log_{10} p_{\text{atm.}}\,[P_2] = 4{\cdot}26 - \frac{23{,}046}{T}$$

$$\log_{10} p_{\text{atm.}}\,[U] = 7{\cdot}80 - \frac{28{,}778}{T}$$

A phosphide $U_2P_3$ has been reported.[237] This was not obtained directly from the elements but by causing phosphine to react with uranium trihydride at 400°C.

Neptunium forms the phosphide $Np_3P_4$ on heating with red phosphorus for 16 hr. at 750°C. in a sealed tube, followed by sublimation of the excess of phosphorus in a

*Table XXII.—Binary Compounds of Phosphorus*

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_nH_{n+2}$<br>$P_nH_n$<br>$P_nH_{n-2}$<br>$P_nH_{n-4}$<br>Others [a] | | | | | | | | | | | | | | | | | He<br>? |
| $Li_3P$<br>$Li_4P_2$<br>$(LiP)$<br>$Li_2P_5$ | $Be_3P_2$ | | | | | | | | | | | $B_{13}P_2$<br>$BP$ | $C_6P_2$<br>$(CP)$ | $P_3N_5$<br>$P_4N_6$<br>$PN$ | $P_4O_{11}$<br>$P_4O_{10}$<br>$P_4O_9/P_4O_8$<br>$P_4O_8/P_4O_7$<br>$P_4O_6$<br>$(P_2O)(PO)$<br>$(P_4O)$ | $PF_5$<br>$PF_3$<br>$P_2F_4$<br>$PF$ | Ne<br>— |
| $Na_3P$<br>$(Na_4P_2)$<br>$(NaP)$<br>$Na_2P_5$ | $Mg_3P_2$ | | | | | | | | | | | $AlP$ | $Si_2P$<br>$SiP$ | $(P_2)$<br>$P_4$ | $(PS_{5-7})$<br>$P_4S_{10}$<br>$P_4S_7$<br>$P_4S_{6-7}$<br>$P_4S_5$<br>$(PS)$<br>$P_4S_3$<br>$(P_4S_2)$ | $PCl_5$<br>$PCl_3$<br>$P_2Cl_4$<br>$(PCl)$ | A<br>— |
| $(K_3P)$<br>$(K_6P_4)$<br>$K_2P_5$ | $Ca_3P_2$<br>$(CaP)$ | $ScP$ | $Ti_3P$<br>$Ti_2P$<br>$Ti_5P_3$<br>$TiP_{0\cdot94}$<br>$TiP$<br>$TiP_2$ | $V_3P$<br>$(V_2P)$<br>$V_3P_2$<br>$VP$<br>$VP_2$ | $Cr_3P$<br>$Cr_2P$<br>$CrP_{0\cdot9}$<br>$CrP$<br>$CrP_2$ | $(Mn_4P)$<br>$Mn_3P$<br>$Mn_2P$<br>$(Mn_3P_2)$<br>$MnP$<br>$MnP_3$ | $Fe_3P$<br>$Fe_2P$<br>$FeP$<br>$FeP_2$ | $(Co_4P)$<br>$Co_2P$<br>$(Co_3P_2)$<br>$CoP$<br>$CoP_3$ | $Ni_3P$<br>$Ni_5P_2$<br>$Ni_2P$<br>$Ni_6P_5$<br>$NiP_2$<br>$NiP_3$ [b] | $Cu_3P$<br>$(Cu_2P)$<br>$(Cu_3P_2$<br>$(CuP)$<br>$CuP_2$ | $Zn_3P_2$<br>$ZnP_2$ | $GaP$ | $GeP$ | $AsP$ | $P_2Se_5$<br>$P_2Se_3$<br>$P_4Se_3$ | $PBr_{17}$<br>$PBr_7$<br>$PBr_5$<br>$PBr_3$<br>$(PBr)$ | Kr<br>— |
| $Rb_2P_5$ | $Sr_3P_2$ | $YP$ | $Zr_3P$<br>$ZrP_{0\cdot92}$<br>$ZrP$<br>$ZrP_2$ | $Nb_3P$<br>$Nb_7P_4$<br>$NbP_{0\cdot95}$<br>$NbP$<br>$NbP_2$ | $Mo_3P$<br>$MoP$<br>$MoP_2$ | Tc<br>— | $Ru_2P$<br>$RuP$<br>$RuP_2$ | $Rh_3P$<br>$Rh_2P$<br>$Rh_4P_3$<br>$RhP_2$<br>$RhP_3$ | $Pd_{4\cdot9}P$<br>$Pd_3P$<br>$Pd_7P_3$<br>(or $Pd_5P_2$)<br>$PdP_2$<br>$PdP_3$ | $Ag_3P$<br>$(Ag_2P)$<br>$AgP_2$<br>$AgP_3$ | $Cd_3P_2$<br>$CdP_2$<br>$CdP_4$ | $InP$ | $SnP_3$<br>$Sn_3P_4$<br>$SnP$<br>$Sn_4P_3$ | Sb<br>— | $P_2Te_3$ | $PI_3$<br>$P_2I_4$<br>$(PI)$ | Xe<br>— |
| $Cs_2P_5$ | $Ba_3P_2$<br>$BaP_2$<br>$BaP_3$ | $LaP$ | $HfP$<br>$HfP_2$ | $Ta_3P$<br>$Ta_2P$<br>$Ta_5P_4$<br>$TaP$<br>$TaP_2$ | $W_4P$<br>$W_3P$<br>$W_2P$<br>$WP$<br>$WP_2$ | $Re_2P$<br>$ReP$<br>$ReP_2$<br>$ReP_3$ | $OsP_2$ | $Ir_2P$<br>$IrP_2$<br>$IrP_3$ | $Pt_{20}P_7$<br>$PtP_2$ | $Au_3P$<br>$(AuP)$<br>$Au_2P_3$ | $(Hg_3P_2)$ | $Tl_3P$<br>$TlP_3$ | $(PbP_2)$ | Bi<br>— | Po<br>— | At<br>— | Rn<br>— |
| Fr<br>— | Ra<br>— | Ac<br>— | $ThP$<br>$Th_3P_4$ | Pa<br>— | $UP$<br>$U_3P_4$<br>$U_2P_3$<br>$UP_2$ | $Np_3P_4$ | $PuP$ | | | | | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| CeP | PrP | NdP | PmP? | SmP | EuP | GdP |
| TbP | DyP | HoP | ErP | TmP | YbP | LuP |

Rare earth elements

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[a] $P_nH_{n+2}$ ($n=1$–6(7)): $P_nH_n$ ($n=2$–9(10)): $P_nH_{n-2}$ ($n=4$–7(8)(10)): $P_nH_{n-4}$ ($n=6$–9); also $P_2H$, $P_5H_2$, $P_9H_4$, $P_9H_3$, $P_{10}H_4$, $P_{10}H_2$, $P_{11}H_6$, $P_{11}H_3$, $P_{12}H_4$, $(P_{14}H)$.

[b] $Ni_7P_3$ (or $Ni_{12}P_5$), $Ni_3P_2$, $NiP$ and $NiP_4$ have also been reported by various workers.

vacuum at 800°C.[238] Plutonium and red phosphorus form PuP when heated in a vacuum or in helium under slightly reduced pressure.[239–40]

The reactions of phosphorus with the rare earth elements have not been exhaustively investigated, but all of them appear to form monophosphides.[241] Samarium reacts at 900°C.,[242] and at 400° to 500°C. in sealed tubes cerium, praseodymium and neodymium combine violently with red phosphorus.[189, 243]

The binary compounds of phosphorus, including those not formed by direct combination of the elements, are shown in Table XXII. The compounds given in parentheses are those on whose existence doubt has been cast, or which exist only under special conditions of temperature or pressure.

A number of ternary compounds, containing phosphorus and formed by direct union of the elements, have been reported. By sintering the components at 700° to 900°C. the compounds CuPS,[244] FePS,[245] CoPS, RhPS, IrPS, RuPS, OsPS, RhPSe, IrPSe, RuPSe and OsPSe have been made.[246, 245] Other compounds, such as PdPS, PtPS, NiPSe, PdPSe, PtPSe, RhPTe, IrPTe and PtPTe, are also considered to be possible.[246] Substances containing phosphorus and arsenic, e.g. PdPAs, PtPAs,[247] and phosphorus and silicon, e.g. $ZnSiP_2$, $CdSiP_2$,[248] have been synthesized in a similar manner.

Polyphosphides such as $HgPbP_{14}$, $CdPbP_{14}$ and $ZnPbP_{14}$ have been made by heating red phosphorus and alloys of lead with mercury, cadmium or zinc, for 8–10 days at 525° to 610°C.[249] Their structures have been discussed.[250]

## MISCELLANEOUS REACTIONS OF PHOSPHORUS

The earlier investigations (Mellor, VIII, 784) into the reaction between white phosphorus and water have been extended to higher temperatures and pressures. The initial observation[251] that small quantities of phosphorous acid are formed on heating at 200°C. in a sealed tube has been confirmed[252]:

$$P_4 + 6H_2O = 2H_3PO_3 + 2PH_3$$

This reaction is slow at 200°C. and goes to completion in 40 hr. at 240°C., in 20 hr. at 290°C. and in 10 hr. or less at 310°C. Above 240°C., increasing amounts of phosphoric acid are formed and the ratio of phosphine to hydrogen produced decreases. The reaction is catalyzed by phosphoric acid and in the presence of 63% of the latter the reaction time is reduced to a minimum of 1 hr. at 310°C. The mechanism proposed is represented by the equations:

$$\begin{aligned} &P_4 + 6H_2O + 6H_3PO_4 = 10H_3PO_3 && t < 250°C. \\ &4H_3PO_3 = 3H_3PO_4 + PH_3 && t > 250°C. \\ &H_3PO_3 + H_2O = H_3PO_4 + H_2 && t > 250°C. \end{aligned}$$

A slower reaction:

$$PH_3 + 4H_2O = H_3PO_4 + 4H_2$$

also occurs and at temperatures above 350°C. there is some evidence for the formation of phosphine according to the equation:

$$P_4 + 6H_2 = 4PH_3$$

At 290°C. under pressures of 40–50 atm., phosphine is formed according to the equation[11]:

$$2P_4 + 12H_2O = 3H_3PO_4 + 5PH_3$$

Surprisingly, phosphine of high purity, containing little hydrogen, is formed by the hydrolysis of finely divided red phosphorus in polyphosphoric acid, at atmospheric pressure and 280–310°C.[327]

White phosphorus reacts with aqueous sodium hydroxide under pressure to give various oxidation products. At 100°C. a slow reaction occurs with sodium hypophosphite as the main product:

$$P_4 + 4NaOH + 4H_2O = 4NaH_2PO_2 + 2H_2$$

At 200° to 300°C. formation of phosphite is rapid when enough 30% sodium hydroxide to form disodium phosphite is present:

$$P_4 + 8NaOH + 4H_2O = 4Na_2HPO_3 + 6H_2$$

With 30% sodium hydroxide and temperatures above 300°C., or with more dilute alkali (e.g., 4% NaOH) at about 250°C., orthophosphate is formed:

$$P_4 + 8NaOH + 8H_2O = 4Na_2HPO_4 + 10H_2$$

At 300°C. or above, and using alkali in excess of requirement for the disodium salt, oxidation of the phosphite is retarded.

The reaction of phosphorus at 200° to 250°C. with sufficient 30% alkali to form monosodium phosphite yields disodium phosphite and some phosphine. Only half of the phosphorus is oxidized to phosphite, the remainder giving red phosphorus which is slowly converted into phosphine.

The formation of phosphate in these reactions occurs through oxidation of phosphine. This is slow at 230°C. but very rapid at 300°C.:

$$2PH_3 + 4NaOH + 4H_2O = 2Na_2HPO_4 + 8H_2$$

Equimolar amounts of hypophosphorous acid and sodium hydroxide (as 30% solution) do not react under pressure at 200°C. but oxidation to phosphate is rapid above 250°C.:

$$NaH_2PO_2 + 2H_2O \overset{>250°C.}{=} NaH_2PO_4 + 2H_2$$

With 2 moles of sodium hydroxide the reaction is complete within a few minutes at 160°C. according to the equation[253]:

$$NaH_2PO_2 + NaOH = Na_2HPO_3 + H_2$$

The oxidation of white phosphorus with moist air under ordinary conditions of temperature and pressure is reported to yield in seven days a product containing approximately 1% of hypophosphorous acid, 18% of phosphorous acid, 6% of hypophosphoric acid and 75% of phosphoric acid.[254]

The reaction of red phosphorus with water at 175° to 420°C. and under 20–530 atm. pressure can be represented by the following equations, of which the first is for the fastest reaction:

$$\begin{aligned} P_4 + (3+n)H_2O &= P_2O_3,nH_2O + 2PH_3 \\ P_2O_3,nH_2O + 2H_2O &= P_2O_5,nH_2O + 2H_2 \\ 2PH_3 + (5+n)H_2O &= P_2O_5,nH_2O + 8H_2 \end{aligned}$$

On prolonged heating only phosphoric acid and hydrogen are formed according to the reaction:

$$P_4 + (10+2n)H_2O = 2P_2O_5,nH_2O + 10H_2$$

In the absence of catalysts oxidation of $P_2O_3$ occurs only at temperatures above 280°C. Compounds of cobalt, nickel, silver, copper and iron have catalytic action but inorganic acids, alkalis and salts have little influence. Nickel nitrate appears to be the most affective, enabling complete oxidation of phosphorus to phosphoric acid to occur in 20 min. at 200°C.[255]

The oxidation of red phosphorus under pressure has been shown to occur in two stages, in the first of which the phosphorus reacts according to the equations:

$$\begin{aligned} P_4 + 6H_2O &= 2H_3PO_3 + 2PH_3 \\ P_4 + 8H_2O &= 2H_3PO_4 + 2PH_3 + 2H_2 \\ P_4 + 12H_2O &= 4H_3PO_3 + 6H_2 \\ P_4 + 16H_2O &= 4H_3PO_4 + 10H_2 \end{aligned}$$

In the second stage the intermediate products are oxidized in the following way:

$$\begin{aligned} H_3PO_3+H_2O &= H_3PO_4+H_2 \\ 4H_3PO_3 &= 3H_3PO_4+PH_3 \\ PH_3+3H_2O &= H_3PO_3+3H_2 \\ PH_3+4H_2O &= H_3PO_4+4H_2 \end{aligned}$$

At 400°C. without a catalyst complete oxidation of the phosphorus occurs and at 280°C. in the presence of 1% NiO as catalyst the reaction is complete in four minutes. Only the first stage of the reaction is affected by the catalyst, maximum yields of phosphoric acid being obtained with a 3:1 ratio of water to phosphorus. At pressures between 100 and 350 atm. the partial pressure of hydrogen has no apparent effect on the reaction velocity.[256] Yellow phosphorus appears to be oxidized under the above conditions with the same velocity as red phosphorus. The phosphoric acid formed is purer, but the hydrogen is contaminated with phosphine.[257]

Under atmospheric pressure the reaction:

$$P_2+5H_2O = P_2O_5+5H_2$$

takes place slowly at 1000°C. in an atmosphere of nitrogen and in the absence of a catalyst. At 650°C. the reaction is rapidly catalyzed by $Fe_3(PO_4)_2$, the quantity of phosphine decreasing at higher temperatures.[258]

Steam oxidizes phosphorus vapour at 1000° to 1200°C. to form $PH_3$, $P_2O_4$, $P_2O_5$ and $H_2$, the main reactions being:

$$\begin{aligned} P_4+8H_2O &= 2P_2O_4+8H_2 \\ P_2O_4+H_2O &= P_2O_5+H_2 \end{aligned}$$

The formation of phosphine is nearly independent of temperature and decreases as the steam/phosphorus ratio is increased. Complete oxidation to $P_2O_5$ and elimination of $PH_3$ formation occurs in the presence of phosphate rock. The calculated equilibrium constant for the second of the above reactions is not in good agreement with experimental results. The latter seem to favour the formation of $P_4O_8$ and $P_4O_{10}$.[259]

Platinum and palladium supported on aluminium metaphosphate or zirconium pyrophosphate are stable and very active catalysts for the reaction[260]:

$$P_4+16H_2O = 4H_3PO_4+10H_2$$

Copper is an active, but less stable, catalyst. Using nitrogen as carrier gas the optimum conditions for over 99% oxidation of the phosphorus to phosphoric acid are 650° to 800°C., steam/phosphorus molar ratio of 16–30, and space velocities of 640–9500/hr. (The space velocity is the volume of $P_4$ gas, water vapour and carrier gas, per unit volume of catalyst.) Traces of phosphine and phosphorous acid are removed by heating the reaction products at 400°C. in a secondary catalyst chamber. At 700°C. with a steam/phosphorus ratio of 22 the percentage of phosphorus present as phosphorous acid in the product is given by the expression:

$$\%\ H_3PO_3 = 1{\cdot}1+6{\cdot}11\times 10^{-4}V$$

where $V$ is the space velocity. The phosphorous acid formed increases with the reaction temperature as shown in Fig. 5.

Some thermodynamic data for the reaction:

$$P_4(g)+16H_2O(g) = 4H_3PO_4(85\%)+10H_2(g)$$

are given in Table XXIII.

Operation of the reaction on a pilot plant scale has been described.[261–2]

Mixtures of carbon dioxide and phosphorus vapour containing more than 11% phosphorus quickly attain equilibrium at 800° to 1200°C. with the conversion of about 80% of the carbon dioxide to monoxide. For mixtures containing less than 11% of phosphorus all the latter is oxidized to phosphorus tetroxide and pentoxide. Calculation of the equilibrium constant from the experimental data suggests that the reactions involved are:

$$P_4+8CO_2 = 8CO+2P_2O_4$$
$$P_2O_4+CO_2 = CO+P_2O_5$$

In the presence of phosphate rock, phosphorus is oxidized completely to metaphosphate under the above conditions.[263]

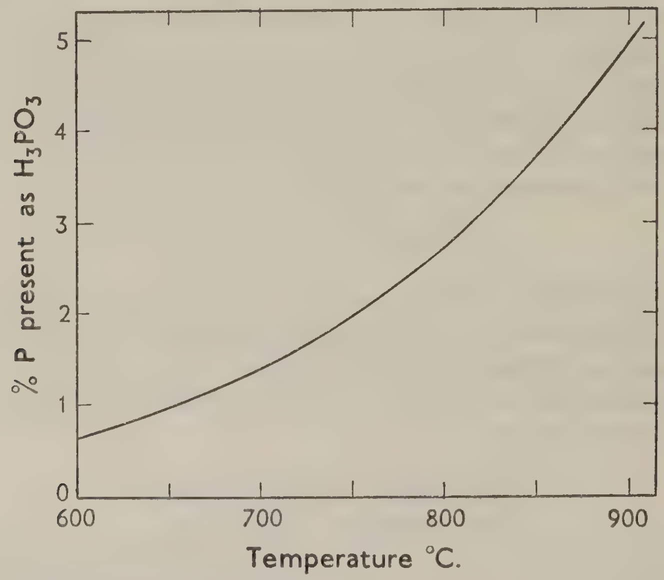

FIG. 5.—Effect of temperature on the amount of trivalent phosphorus in the oxidation of phosphorus vapour with steam

Under controlled conditions phosphorus vapour can be oxidized to phosphorus pentoxide in the presence of carbon monoxide. For mixtures containing 1% of phosphorus, 40% of carbon monoxide and 59% of nitrogen, and using 1·65 times the amount of air required to oxidize the phosphorus, a negligible amount of carbon monoxide is oxidized at 600°C. With higher concentrations of phosphorus (7% P, 85–92% CO) at 700°C. and using 25% excess of air, 22% of the carbon monoxide is oxidized. A greater excess of air and higher temperatures increase the amount of carbon monoxide oxidized and at 900°C. oxygen is consumed so fast in this reaction that the phosphorus oxidation is incomplete. Preferential oxidation of the phosphorus is increased by adding sufficient water vapour to the system to give metaphosphoric acid as the end product.[264]

*Table XXIII.—Thermodynamic Data for the Oxidation of Phosphorus Vapour with Steam*[260]

| Temp. °C. | $-\Delta H$ g.-cal./mole | $-\Delta G$ g.-cal./mole | $K$ (pressures in atm.) |
|---|---|---|---|
| 25 | 300,100 | 198,650 | $4{\cdot}98\times10^{145}$ |
| 100 | 292,400 | 174,000 | $9{\cdot}14\times10^{101}$ |
| 200 | 279,650 | 143,800 | $2{\cdot}75\times10^{66}$ |
| 300 | 263,900 | 117,500 | $2{\cdot}87\times10^{44}$ |
| 500 | 225,200 | 70,800 | $1{\cdot}08\times10^{20}$ |
| 700 | 175,900 | 36,600 | $1{\cdot}65\times10^{8}$ |
| 727 | 168,500 | 32,800 | $1{\cdot}50\times10^{7}$ |
| 827 | 139,500 | 20,640 | $1{\cdot}27\times10^{4}$ |
| 1000 | 83,600 | 6,000 | 10·8 |
| 1100 | 55,400 | 1,200 | 1·56 |

The air-oxidation at 20°C. and at atmospheric pressure of solid phosphorus deposited on ground quartzite is reported[265] to give the oxides $P_4O$, $P_4O_2$, $P_4O_6$ and $P_4O_{10}$. This reaction is complete in less than five minutes, but is preceded by an activation period which depends on the amount of phosphorus involved. The activation time is 30 min. when 1·3% of phosphorus is deposited on the quartz, and increases to 36 hr. when the amount of deposit is 0·85%. The $P_4O/P_4O_{10}$ ratio in the product is always 2:3. Ozone eliminates the induction period and the product then contains only $P_4O_6$ and $P_4O_{10}$.

The slow oxidation of moist yellow phosphorus in the presence of charcoal at room temperature gives a mixture of acids containing approximately 3% $H_3PO_2$, 0–14% $H_3PO_3$, 10–25% $H_4P_2O_6$ and 63–77% $H_3PO_4$.[266]

The heterogeneous catalysis of the reaction of phosphorus with water has been discussed.[267] If aqueous suspensions of phosphorus are exposed to light for up to a year, phosphorous acid, some phosphoric acid and traces of hypophosphorous acids are formed and a residue of red phosphorus remains. The transformation of yellow to red phosphorus seems to be the main reaction. The following reactions can then occur[268]:

$$\begin{aligned} 4P+6H_2O &= 3H_3PO_2+PH_3 \\ 2H_3PO_2 &= H_3PO_4+PH_3 \\ PH_3+O_2 &= HPO_2+H_2 \\ 4H_3PO_3 &= 3H_3PO_4+PH_3 \end{aligned}$$

The oxidation of phosphorus in liquid iron at 1500° to 1650°C. has been studied by adding phosphorus, in an atmosphere of water vapour and hydrogen, to molten iron containing 0·02% C, 0·01% Mn, 0·01% Ni, 0·007% Cr and 0·002% S.[269] With 1·2% or less of phosphorus in the system the reaction is:

$$2P(g)+3Fe(l)+8H_2O(g) = (FeO)_3P_2O_5(l)+8H_2(g)$$

for which the free energy and equilibrium constant are given by[270]:

$$\Delta G = 26{\cdot}6T-125{,}500$$

$$\log_{10} K = \frac{27{,}400}{T} - 58$$

At phosphorus contents of 1·2 to 3·0% the reaction is:

$$4P(g)+3Fe(l)+13H_2O(g) = (FeO)_3P_2O_5(l)+13H_2(g)+P_2O_5$$

and the free energy and equilibrium constant are given by:

$$\Delta G = 77{\cdot}95T-111{,}600$$

$$\log_{10} K = \frac{24{,}400}{T} - 17{\cdot}0$$

For the reaction:

$$4P(g)+13O(g)+3Fe(l) = (FeO)_3P_2O_5(l)+P_2O_5$$

the corresponding data are:

$$\Delta G = 226{\cdot}5T-531{,}000$$

$$\log_{10} K = \frac{118}{T} - 58{\cdot}2$$

The free energy of the reaction:

$$2P(g)+5H_2O(g) = P_2O_5(g)+5H_2(g)$$

is given by:

$$\Delta G = 13{,}900-51{\cdot}37T$$

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For phosphorus–oxygen equilibria in molten iron systems it has been shown that in the temperature range 1540° to 1580°C. the free energy of the reaction:

$$2[P]+5H_2O(g)+4CaO(s) = Ca_4P_2O_9(s)+5H_2(g)$$

as calculated from the expression:

$$\Delta G^\circ = 0{\cdot}0729T-187{\cdot}9 \text{ kcal.}$$

agrees closely with experimental data.[271]

The equilibrium constant,

$$K_p = \frac{(FeO)^5[\Sigma P]}{[Fe]^5(P_2O_5)}$$

where concentrations are in percentage by weight, for the reaction:

$$5FeO+2P = P_2O_5+5Fe$$

is 0·056 at 1450°C. and 0·091 at 1525°C. for the ternary Fe–P–O system containing 4–5% P. Magnesium and calcium oxides lower the value of $K_p$ but $SiO_2$ increases it.[272]

The oxidizing and combustion properties of white[273] and red[274] phosphorus have been used to produce chemical smokes,[275] incendiaries[276] and flame throwers.[277]

Red phosphorus is oxidized by ceric sulphate in the presence of phosphoric acid. The reaction is bimolecular and between 30° and 60°C. has a temperature coefficient of 1·46 for every 10°C. rise in temperature. At 32° to 42°C., 37° to 47°C. and 47° to 57°C. the activation energies are 7404, 7502 and 7765 g.-cal., respectively. The mechanism suggested for the reaction is[278]:

$$\begin{aligned} 2Ce(SO_4)_2+H_2O &= Ce_2(SO_4)_3+H_2SO_4+O \\ 2P+5O &= P_2O_5 \\ P_2O_5+3H_2O &= 2H_3PO_4 \end{aligned}$$

In acid solutions of potassium permanganate the reaction is[279]:

$$P+MnO_4^- = PO_4^{3-}+Mn^{2+}$$

Refluxing red phosphorus for 6–8 hr. in N sulphuric acid with 5–10 times its weight of potassium chlorate oxidizes 90% of the phosphorus:

$$6P+5KClO_3+9H_2O = 6H_3PO_4+5KCl$$

Small amounts of manganous sulphate catalyze the reaction to some extent.[280]

Red phosphorus is quantitatively oxidized by refluxing for 1 hr. with an acid (0·5N $H_2SO_4$) solution of potassium bromate[281]:

$$6P+6KBrO_3+3H_2SO_4+6H_2O = 6H_3PO_4+3Br_2+3K_2SO_4$$

At 30° to 55°C. the reaction is bimolecular with respect to bromate.[282] A second order reaction is reported for the oxidation of phosphorus with acid solutions containing one mole of bromine to five moles of bromate[283]:

$$5Br^-+BrO_3^-+6H^+ = 3Br_2+3H_2O$$

A similar but slower oxidation, requiring 3 hr. heating under reflux, occurs with potassium iodate[284]:

$$6P+6KIO_3+3H_2SO_4+6H_2O = 6H_3PO_4+3I_2+3K_2SO_4$$

This reaction is a composite one; the first stage:

$$5P+3IO_3^-+3H^++6H_2O = \tfrac{3}{2}I_2+5H_3PO_3$$

is slow and also produces some phosphate. This is followed by a rapid oxidation:

$$2P+3I_2+6H_2O = 6H^++6I^-+2H_3PO_3$$

The oxidation of the phosphite by iodate ion is very slow:

$$5H_3PO_3 + 2IO_3^- = I_2 + 3H^+ + 5H_2PO_4^- + H_2O$$

and the rate-determining step, which is catalyzed by hydrogen ions, is probably given by:

$$H_3PO_3 + I_2 + H_2O = 3H^+ + 2I^- + H_2PO_4^-$$

This reaction is somewhat faster than that involving iodate ions.[284]

The oxidation of red phosphorus by iodine in potassium iodide solution is bimolecular with a temperature coefficient of 4·101–3·198 at 20° to 35°C., the activation energy being 25,870–24,370 g.-cal.[285] Complete oxidation of the phosphorus takes place in 24–30 hr. at room temperature when the phosphorus to iodine molar ratio is 1:4. At 60°C. and a molar ratio of 1:3 the reaction is complete in 10 hr. The equation for the oxidation is inferred to be[286]:

$$2P + 3I_2 + 6H_2O = 2H_3PO_3 + 6HI$$

Oxidation with periodate according to the equation:

$$14P + 10KIO_4 + 5H_2SO_4 + 16H_2O = 14H_3PO_4 + 5K_2SO_4 + 5I_2$$

takes place quantitatively on heating under reflux for 4–5 hr. in 0·05–2·0N $H_2SO_4$ solution using a molar $KIO_4$:P ratio of 5:7.[287] In 0·5N $H_2SO_4$ this oxidation is of second order. The velocity constant $K$ was calculated from the equation:

$$K = tC_\alpha \log_e \frac{C_t(C_0 - C_\alpha)}{C_0(C_t - C_\alpha)}$$

where $t$ is the time in minutes, $C_0$ is the initial $KIO_4$ concentration, and $C_t$ and $C_\alpha$ are the concentrations at time $t$ and $\alpha$, respectively. Values of $K$ are given in Table XXIV when the initial concentration is N/15 $KIO_4$.[288]

*Table XXIV.—Oxidation of Red Phosphorus by Potassium Periodate*[288]

| Temperature °C. | Velocity constant $K \times 10^4$ mole/l./min. |
|---|---|
| 25 | 2·63 |
| 30 | 4·45 |
| 35 | 6·15 |
| 40 | 8·55 |

The oxidation of phosphorus by $XO_3^-$, $XO_4^-$, $X^-$–$XO_3^-$ mixtures and by $X^-$–$XO_4^-$ mixtures, where X is a halogen, has been summarized as follows.

The primary reaction with $XO_3^-$ or $XO_4^-$ in acid solution slowly forms $X_2$, phosphorous acid, and a small quantity of phosphate. A rapid secondary reaction of phosphorus with $X_2$ forms phosphorous acid initially and a further slow reaction then yields phosphoric acid and $X^-$. This last oxidation is the rate-determining step.

Mixtures of $X^-$–$XO_3^-$ and $X^-$–$XO_4^-$ liberate $X_2$ instantaneously and quantitatively in acid solution and the main oxidizing reaction is between $X_2$ and phosphorus. The rate of reaction of phosphorus increases with increasing concentration of oxidizing agent and with the temperature. Increase in temperature, however, causes volatilization of $X_2$. High concentrations of HCl and $NO_3^-$ interfere with the reaction. The most suitable acidity is 0·5–2·0N $H_2SO_4$.[289]

The reaction between phosphorus and iodine in carbon tetrachloride has been discussed on page 247. This has been modified and applied as a reduction process in organic chemistry. A number of organic compounds can be reduced at temperatures below 100°C., using phosphorus and potassium iodide with hydrochloric acid as diluent. For temperatures up to 150°C. phosphoric acid of sp. gr. 1·7 may be used,

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but sulphuric acid is unsuitable because it is reduced by the hydrogen iodide formed in the reaction.[290]

Molten iodine bromide reacts violently with phosphorus to form tri- and pentabromides.[291] A similar reaction occurs with iodine monochloride to form iodine and phosphorus pentachloride.[292]

The oxidation of elemental phosphorus with copper nitrate and similar reagents to form hypophosphoric acid is discussed in Section XXII. In the treatment of phosphorus burns with cupric salts the action of the latter is fastest at pH 10.[293]

Phosphorus heated in the dry state with alkaline-earth hydroxides and alkali metal nitrates forms ammonia, phosphine and hydrogen. When excess of nitrate is present in the mixture, nitric oxide, but no ammonia, results.[294] Magnesium, calcium or barium hydroxide forms phosphine free from diphosphine, $P_2H_4$.[295] Lithium hydroxide yields phosphine and $Li_3PO_4$.[296]

Red phosphorus reacts at room temperature with nitryl fluoride to form nitryl hexafluorophosphate. The reaction appears to proceed in the following stages[297]:

$$\begin{aligned} P+5NO_2F &= PF_5+5NO_2 \\ PF_5+NO_2F &= NO_2PF_6 \end{aligned}$$

White phosphorus and nitrososulphuryl fluoride react to give nitrosoyl hexafluorophosphate, $NOPF_6$.[298] Sulphuryl chloride converts phosphorus into phosphorus trichloride, red phosphorus being apparently more easily chlorinated than the white form.[299] The latter explodes with selenium monochloride,[300] reacts violently with selenium tetrafluoride and inflames in contact with selenium oxyfluoride.[301] Small amounts of white phosphorus dissolve in vanadium oxytrichloride without apparent reaction but in larger proportions an explosive reaction occurs at temperatures below 100°C.[302]

A slow reaction takes place, with formation of $P_2H_4$, when a concentrated aqueous solution of potassium hydroxide is added at room temperature to a solution of white phosphorus in glycerol. A yellow precipitate with the composition $P_5H_2$ is deposited on standing for several days.[303]

Red phosphorus with sulphur has been used in the polymerization of $\alpha$-olefins to form synthetic lubricants.[304] This has been applied to olefins containing 6 to 14 carbon atoms, at temperatures of 250° to 450°C. and pressures up to 280 atm.[305] Black phosphorus itself has also been suggested as a lubricant additive.[307]

An ether solution of white phosphorus forms colloidal gold when heated with chloroauric acid ($HAuCl_4$) in the presence of potassium hydroxide.[306]

An excellent review of the organic reactions of elemental phosphorus has appeared.[308] These reactions fall into three broad classes: the reactions of phosphorus with nucleophilic compounds such as organometallic derivatives; those with electrophilic compounds (e.g. alkyl halides); and those with alcohols or alkenes, which occur under oxidizing conditions. The products are often complex in nature, and good yields of individual compounds are seldom obtained.

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### SECTION VI

# PHOSPHORUS HYDRIDES AND PHOSPHONIUM COMPOUNDS

### BY E. J. LOWE

## PREPARATION

Phosphine is reported to be a major product of the hydrolysis of phosphorus triiodide[1] and a minor product of the hydrolysis of phosphorus tribromide[1] and triphosphorus hexaoxydi-iodide.[161] A mixture of phosphine and hydrogen is obtained by the reaction of phosphorus with dry alkaline earth hydroxides[2] and lithium hydroxide.[3] Phosphine and sodium hypophosphite are obtained in higher yield and greater purity by reacting white phosphorus with sodium hydroxide in 70% v/v methanol/water mixtures instead of in water.[162] The reaction of phosphorus with steam, the main product of which is phosphoric acid, yields phosphine as a by-product,[4–7] the best yield being obtained from the reaction under pressure at the relatively low temperature of 300°C. and in the absence of any catalyst. All of the phosphorus present in the gases from a phosphorus blast furnace can be converted to phosphine by blowing steam through the furnace[8]; it is suggested that reaction occurs between the phosphorus and active hydrogen. Phosphine has also been produced by passing phosphorus vapour and steam through a bed of coke at 700–1000°C.,[9] and is evolved on heating white or red phosphorus under aqueous phosphoric acid, zinc chloride and calcium chloride solutions at atmospheric pressure and temperatures above 170°C.[9]

The thermal decomposition of sodium hypophosphite to give phosphine has been followed thermogravimetrically.[10] The other products are claimed to be sodium pyrophosphate and sodium metaphosphate, which at temperatures above 300°C. recombine giving sodium triphosphate[163]:

$$5NaH_2PO_2 \rightarrow Na_5P_3O_{10} + 2PH_3 + 2H_2$$

It is suggested[11] that phosphine is formed in the thermal decomposition of calcium phosphite by the reduction of phosphite or phosphate with hydrogen. Alkali metal phosphites or hypophosphites decompose in the presence of phosphoric acid at 190° to 400°C., giving phosphine and a phosphite-free glassy polyphosphate residue.[225] Phosphine is produced by the reduction of ammonium phosphates, orthophosphoric acid and metaphosphoric acid with hydrogen at temperatures above 600°C.[12–3] The reduction of metaphosphoric acid by natural methane at 1050°C., however, gave mostly phosphorus and only a minor amount of phosphine.[164]

Elemental phosphorus and hydrogen do not combine at normal temperatures and pressures to form phosphine,[14] but it can be prepared by rapidly cooling the reaction products of phosphorus with hydrogen energized by a high current arc.[15] Good yields of phosphine are obtained by causing phosphorus trichloride to react with lithium aluminium hydride in the presence of diethyl ether at temperatures below 0°C.,[16] but only a 0·25% yield is obtained at 75°C. in the absence of diethyl ether. However, lithium hydride is claimed to give commercially acceptable yields of phosphine under these conditions.[226] The reduction of phosphites or hypophosphites by sodium borohydride in acid solution also gave only traces of phosphine.[165]

Phosphine is liberated at the anode in the electrolysis of sodiophosphine and potassiophosphine in liquid ammonia,[17] the anode reaction being

$$6PH_2^- + 2NH_3 - 6e^- = 6PH_3 + N_2$$

It is evolved from the electrolysis of vanadium pentoxide in an acid sodium phosphate melt,[18] and it is claimed[19] that phosphine is liberated from a mercury cathode in the electrolysis of an aqueous solution containing sulphuric acid, potassium sulphate and an oxide of phosphorus, and it is also obtained in good yield from the electrolysis of an aqueous acid in the presence of white phosphorus.[20]

Some phosphine is formed by the acid hydrolysis of indium phosphide.[166] A safe laboratory procedure for the preparation of phosphine is the hydrolysis of aluminium phosphide in an inert liquid miscible with water.[167] The reaction of hydrochloric acid with a boiling alcoholic suspension of aluminium or zinc phosphide gives phosphine free from diphosphine or acetylene.[168] Excellent yields of phosphine of high purity can be obtained by reacting finely divided amorphous phosphorus, made by partial conversion of yellow phosphorus, with polyphosphoric acid and steam at temperatures above 250°.[227] Phosphine containing little hydrogen and free from diphosphine is obtained on heating an aqueous acid above zinc amalgam in the presence of white phosphorus.[9]

The formula, $P_2H_4$, for liquid diphosphine has been confirmed by careful determination of its molecular weight.[21] No evidence of higher homologues was obtained from the reaction between white phosphorus and aqueous potassium hydroxide.[21] A yellow precipitate of composition $P_5H_2$ was obtained from the reaction of white phosphorus in glycerol with concentrated aqueous potassium hydroxide.[22] At room temperature in an anhydrous sealed system diphosphine, $P_2H_4$, decomposes with evolution of phosphine to form a yellow solid of composition close to $P_9H_4$, but in the presence of moisture substances of composition close to $P_{12}H_6$ are formed.[23] When $P_2H_4$ is heated phosphine is evolved to yield non-stoicheiometric solid hydrides having H:P ratio less than 4:9.[23]

More recently a whole series of higher linear and cyclic phosphine hydrides (phosphanes) has been detected, as resulting from the pyrolysis of diphosphine (diphosphane), or the careful hydrolysis of calcium phosphide. They can be separated by fractional condensation or crystallization at $-30$ to $-78$°C.[219–21] or by gas-liquid chromatography on a kieselguhr/silicone oil column at 60°C.[220] and identified by mass spectrography. Only $P_3H_5$ is at present known in a reasonably pure state,[219] as a white solid stable at $-23$° but decomposing without melting when warmed, to give phosphine and a yellow solid, possibly $P_2H$. Higher homologues which have been obtained in the form of fairly highly enriched fractions are shown below, together with diphosphorus dihydride (diphosphane-2) so far only detected by a mass spectrum peak in the products of pyrolysis of $P_2H_4$ at 0·1 torr and 300–400°K.[222]

| | $P_nH_{n+2}$ | $P_nH_n$ | $P_nH_{n-2}$ | $P_nH_{n-4}$ | Others |
|---|---|---|---|---|---|
| Diphosphanes | $\mathit{P_2H_4}$ | $\mathrm{P_2H_2}$ | | | |
| Triphosphanes | $\mathit{P_3H_5}$ | $\mathit{P_3H_3}$ | | | |
| Tetraphosphanes | $\mathit{P_4H_6}$ | $\mathit{P_4H_4}$ | $\mathrm{P_4H_2}$ | | |
| Pentaphosphanes | $\mathrm{P_5H_7}$ | $\mathit{P_5H_5}$ | $\mathit{P_5H_3}$ | | |
| Hexaphosphanes | $\mathrm{P_6H_8}$ | $\mathrm{P_6H_6}$ | $\mathit{P_6H_4}$ | $\mathrm{P_6H_2}$ | |
| Heptaphosphanes | $[\mathrm{P_7H_9}]$ | $\mathrm{P_7H_7}$ | $\mathrm{P_7H_5}$ | $\mathit{P_7H_3}$ | |
| Octaphosphanes | | $\mathrm{P_8H_8}$ | $[\mathrm{P_8H_6}]$ | $\mathit{P_8H_4}$ | |
| Nonaphosphanes | | $\mathrm{P_9H_9}$ | | $\mathrm{P_9H_5}$ | $\mathit{P_9H_3}$ |
| Decaphosphanes | | $[\mathrm{P_{10}H_{10}}]$ | $[\mathrm{P_{10}H_8}]$ | | $\mathit{P_{10}H_4}$, $\mathrm{P_{10}H_2}$ |
| Undecaphosphanes | | | | | $\mathit{P_{11}H_6}$, $\mathrm{P_{11}H_3}$ |
| Dodecaphosphanes | | | | | $\mathrm{P_{12}H_4}$ |
| Tetradecaphosphanes | | | | | $[\mathrm{P_{14}H}]$ |

Italicized formulae are of compounds especially favoured at a particular value of $n$, while those in brackets are doubtful at present. There is a clear tendency for cyclic and condensed phosphanes of lower hydrogen content to be favoured over linear phosphanes, with increasing values of $n$. The higher phosphanes are volatile materials, decomposing slowly at 0°C. in the dark and rapidly at room temperature in daylight, to phosphine and solid yellow compounds of high P content.[221] A nomenclature similar to that of the boranes has been suggested: e.g. $P_3H_3$ = triphosphane-3, $P_9H_4$ = nonaphosphane-4.[220] From the shift of the appearance potential of the $P_2H_2^+$ peak between 300 and 430°K., the standard heat of formation of $P_2H_2$ has been calculated as $+26 \pm 5$ kcal./mole.[222]

In contact with boiling ammonia, diphosphine decomposes with evolution of phosphine to yield an ammonia-soluble black residue of variable composition in the P:H ratio range of 3·05–4·81:1 and $NH_3$:H range of 0·09–0·92:1.[24] With liquid ammonia the solid hydride $P_9H_2$ gives an amorphous product of composition $P_9H_{1\cdot38}(NH_3)_x$.[25] A solid phosphorus hydride was obtained from the reaction of a cobalt–tin–phosphorus alloy with concentrated hydrochloric acid.[26]

Phosphorane, $PH_5$, is not found among the hydrogenation products of phosphorus pentachloride with excess of lithium borohydride at $-80°$ or lithium aluminium hydride at $-100$°C.[188] In the latter case only phosphine and hydrogen are found. Similarly the only phosphorus-containing products from the reduction of phosphoryl bromide or chloride with lithium hydride, aluminium hydride or lithium aluminium hydride are phosphine and the solid polymeride $(PH)_n$. Although phosphine oxide was not isolated it may be an intermediate:

$$POCl_3 \rightarrow [PH_3O] \rightarrow [PH_2OH] \rightarrow (PH)_n$$

This suggestion is supported by the isolation of a white crystalline adduct, $PH_3OBH_3$, when lithium borohydride is used for the reduction. The adduct was stable at $-115°$, but decomposed at $-90°$, evolving hydrogen, and giving a viscous polymer $PH_2OBH_2$.[189] A kinetic study of the oxidation of phosphine by hypochlorite suggested that the formation of phosphine oxide was a rate determining step, but that its subsequent oxidation was very fast.[190]

By treatment of phosphine with bromine, phosphorus pentabromide and phosphorus pentachloride, the existence of such partially halogenated phosphines as $PH_4Br$, $PH_2Br$ and $PH_2Cl$ was indicated but not definitely established.[27] A laboratory preparation of phosphonium iodide, $PH_4I$, has been described.[28, 191] Phosphonium perchlorate has been prepared[159–60] by passing phosphine through cold aqueous perchloric acid. The salt is very explosive and could not be obtained dry, its composition being given as $PH_3,HClO_4$[159] and $2PH_3,3HClO_4$.[160] The analogous preparation of phosphonium perrhenate was unsuccessful.[160]

## PHYSICAL PROPERTIES OF PHOSPHINE

Transitions in solid phosphine have been reported at temperatures $30{\cdot}3_2°$, $88{\cdot}5_3°$ and $139{\cdot}6_6$°K. (melting point),[29, 30] at 30·29°, 49·43° and 88·10°K.[31] with heats of transition of 19·6, 185·7 and 115·8 g.-cal./mole, respectively, and at 139·35°K. (m.p.)[31] under the triple-point pressure of 27·33 mm. Hg with heat of fusion of 270·4 g.-cal./mole. A test of the third law of thermodynamics is made possible by evaluation of the entropy of two crystalline forms of this substance because of the slow conversion of the unstable to the stable form of solid phosphine at 49·43°K. The entropy of the stable and unstable forms at 49·43°K. is 8·14 and 8·13 g.-cal./degree/mole, respectively.[31] There is a region of abnormally high heat capacity in the supercooled solid between 30·29 and 35·66°K.[31] The change in volume on melting has been studied.[32] Calculation of the molar volume of liquid and solid phosphine gave 44·08 and 41·83 c.c., respectively, at the triple point 139·41 ± 0·05°K. The experimentally determined heat of vaporization at the b.p. (760 mm. Hg) is given as 3492 ± 4 g.-cal./mole at 185·7°K.,[30] 3489 ± 3 g.-cal./mole at 185·38°K.,[31] and 3493 ± 3 g.-cal./mole at 185·72°K.[33] Vapour pressure curves are given[31] for solid phosphine in the temperature range 128·67–139·35°K. as $\log_{10} P(\text{mm.}) = 7{\cdot}86434 - 895{\cdot}700/T$, and for liquid phosphine in the temperature range 139·35–185·56°K. as

$$\log_{10} P(\text{mm.}) = 10{\cdot}73075 - 1027{\cdot}300/T - 0{\cdot}0178530T + 0{\cdot}000029135T^2$$

which gives the heat of vaporization at the boiling point as 3472 g.-cal./mole. On the basis of the significant structure theory of liquids, the vapour pressure, molar heat capacity, molar volume and entropy of liquid phosphine have been calculated over the range 140–185°K. and show good agreement with observed values.[230] The surface tension of liquid phosphine calculated by the same authors also agreed well with previous data.[52] The entropy of vaporization of phosphine has been related to the internal order within the liquid.[34] The entropy of phosphine gas at the b.p. has been determined from experimental thermal data to be 46·39[30] and 46·39 ± 0·1[31] g.-cal./degree/mole, and calculated[30] from structural and spectroscopic data to be 46·43 g.-cal./degree/mole. The entropy at 298·1°K. is 50·35[31] g.-cal./degree/mole from thermal data and 50·5 ± 0·1,[35] 50·20,[36, 169] 50·22[170] and 50·23[37] g.-cal./degree/mole from spectroscopic data. Values of heat content $H^\circ$, free energy $G^\circ$ and heat capacity $C_p^\circ$ are also given for $PH_3$ and $PD_3$ over a range of temperatures.[169] Values of the heat capacity at constant pressure $C_p^\circ$, the entropy $S^\circ$, and the free energy function, $-(\phi^\circ - H_0^\circ)/T$, have been calculated for the molecules $PH_2D$, $PHD_2$, $PH_2T$, $PHT_2$, $PDT_2$ and PHDT over the temperature range 298·2 to 1000°K.[218] The entropy of the phosphonium ion, $PH_4{}^+$, is calculated from spectroscopic data to be 48·82 g.-cal./degree/mole at 298·16°K.[37]

## Thermodynamic Properties

Experimental determinations of the equilibrium $4P_{red} + 6H_2 \rightleftharpoons 4PH_3$ have been made[38] over the temperature range 627–771°K. and the data obtained have been analysed.[35–6, 216] For the gas phase reaction $P_4(g) + 6H_2(g) = 4PH_3(g)$

$$K_p = P^4_{PH_3}/P_{P_4} \times P^6_{H_2}$$

is $1 \times 10^{-11}$ atm.$^{-3}$ at 627°K. and $1{\cdot}9 \times 10^{-12}$ atm.$^{-3}$ at 771°K. Calculation for 298·1°K. gives the standard free energy change for the reaction

$$P_{(\text{solid, white})} + \tfrac{3}{2}H_2(g) = PH_3(g)$$

as $\Delta G^\circ_{298\cdot 1} = -3140$ g.-cal./mole, which indicates that thermodynamically there is a tendency for white phosphorus and hydrogen to combine to form phosphine although the rate of the reaction is not appreciable below about 300°C. For the reaction $P_4(g) + 6H_2(g) = 4PH_3(g)$, $\Delta H_0^\circ$ is estimated as $+1530$ g.-cal. Values of $(H^\circ - H_0^\circ)$ and $-(G^\circ - H_0^\circ)/T$ are tabulated for phosphine over the temperature range 298·1–1500°K.[36, 224] Tables of heat capacity, entropy, reduced isobaric-isothermal potential and reduced enthalpy have been calculated for phosphine over the temperature range 298–1000°K.[39] For phosphine gas, using the best thermodynamic data,[36] the constants in the empirical heat capacity equation $C_p = a + bT + cT^2$ are $a = +4{\cdot}496$, $b = +0{\cdot}014372$ and $c = -0{\cdot}000004072$.[40] This equation gives maximum deviation 0·29% and mean deviation 0·13% in the temperature range 298·1–1500°K. There is some uncertainty about the heat of formation of phosphine. The equilibrium data[38] give $\Delta H_f^\circ$ as $-2360$ g.-cal./mole, but this value is subject to a wide spread. Values of $-2300$[41] and $+2210$[42] g.-cal./mole are quoted. A direct determination[43] of the heat of formation of phosphine and diphosphine by examining the explosive decomposition of the hydrides in admixture with stibine, $SbH_3$, gave for phosphine, $PH_3$, $\Delta H_f^\circ = +1300 \pm 400$ g.-cal./mole, and for diphosphine, $P_2H_4$,

$$\Delta H_f^\circ = +5000 \pm 1000 \text{ g.-cal./mole}$$

From values of appearance potentials of various positive ion species in the mass spectra of phosphine and diphosphine, heats of formation have been calculated[171] for phosphine, $PH_3$, $\Delta H_f^\circ = 2300$ g.-cal./mole and for diphosphine, $P_2H_4$,

$$\Delta H_f^\circ = 9900 \text{ g.-cal./mole}$$

The thermochemistry of phosphine and phosphonium compounds has been discussed.[172, 224]

### Density, Critical Constants, Etc.

From a careful study of the density and compressibility of phosphine, the atomic weight of phosphorus was found to be 30·977.[44–5] The normal density of gaseous phosphine $L_0^{760}$ is 1·5307 g./l. and the factor for the compressibility between zero and 1 atm. pressure is $(1+\lambda)=1{\cdot}0091$.[45] The normal density of gaseous phosphine derived from the actual density measured between zero and 1 atm. satisfies an equation[46] of the form $L_p$ (g./l.) $=a+b_p$, where $a=1{\cdot}516817$ and $b=0{\cdot}013938$ for $p=1$ atm.

Certain relations between the critical constants of the inert gases and of gaseous hydrides, including phosphine, have been derived.[47] An isotope effect has been demonstrated by comparing the critical temperatures of phosphine, $PH_3$ (325·1°K.) and trideuterophosphine, $PD_3$ (323·6°K.).[173] Values of the critical constants for liquid phosphine calculated on the basis of the significant structure theory of liquids show reasonable agreement with observation.[230]

Data of state were determined for phosphine in the temperature range 190–300°K. and the experimental values of the secondary virial coefficient $B$ in the equation $PV_m=RT+BP$ were calculated.[48] $B$ can be expressed in terms of a power series in $1/T$ and ranges from $-452{\cdot}3$ c.c. at 189·9°K. to $-152{\cdot}6$ c.c. at 296·95°K. Good agreement is obtained with values of $B$ computed from critical data using Berthelot's equation, which shows that this equation can be used without serious error. The equation $p=[CT/(v+B)]-[A/(T(v+B)^2)]$ for the line of saturation of liquids and vapours has been derived and compared with van der Waals' equation, and the constants $A$ and $B$ have been determined from critical data for many compounds including phosphine.[49] The regular boiling-point relation between phosphine and the alkylphosphines indicates that phosphine is not associated.[50] Also comparison with the hydrides of neighbouring elements in the Periodic Table shows little or no evidence of hydrogen bonding,[51] although the physical properties of phosphine indicate that there may be some association in the liquid.[52] The degree of gas imperfection $\beta$ in the equation $PV/RT=1+\beta/V$ has been evaluated for several gases.[53] For phosphine $\beta=379$ at a b.p. of 185·35°K. or 143 at a b.p. of 185·72°K., giving $N_2/N_1=0{\cdot}038$ and 0·032, respectively, as the ratio of double to single molecules present in the gas at 1 atm. pressure.

Adsorption isotherms have been obtained for phosphine on both activated carbon and silica gel.[54–6] Adsorption of phosphine by cupric oxide-coated carbon[57] and by potassium benzenesulphonate[58] has also been studied. The dielectric constant for phosphine is 1·003373 at $-47$°C., 1·002381 at 16°C. and 1·001687 at 100°C.[59] The observed dipole moment (0·55 D.,[59] $0{\cdot}578\pm0{\cdot}010$ D.[182]) can only be explained by assuming the participation of the lone pair electrons on phosphorus in *sp* type hybridized orbitals.[174] The diamagnetic susceptibility of phosphine is $-26{\cdot}2\times10^{-6}$ c.g.s. units/mole.[175] Critical potentials have been determined for the ionization and dissociation of phosphine by electron bombardment, and the ions produced have been examined using a mass spectrometer.[60–1, 176]

The intense ultra-violet absorption of phosphine and deuterophosphine in the 1850–2500 A. region[177–8] shows a band structure which can be explained on the assumption that the upper state of $PH_3$ and $PD_3$ is pyramidal, with a barrier to inversion so low that all observed transitions are to levels well above the barrier.[179] The infra-red spectrum[180–1] and the microwave spectrum[182–3] of phosphine and deuterophosphine have also been recorded. The phosphorus nuclear magnetic resonance spectrum of liquid phosphine at $-90°$ shows the expected 1–3–3–1 quadruplet, of chemical shift $+238\pm1$ p.p.m. (relative to 85% $H_3PO_4$).[184] Calculated values of the vibration frequencies (cm.$^{-1}$) in the phosphine and trideuterophosphine molecules are in good agreement with observation, and force constants have been derived.[231]

## PROPERTIES OF DIPHOSPHINE AND PHOSPHONIUM HALIDES

Diphosphine melts at $-99$°C.[21] Vapour pressure data have been obtained for diphosphine[61, 21] which may be expressed[23] as $\log_{10} P(\text{mm.})=7{\cdot}330-1498/T$ in the temperature range 195–290°K.; tetradeuterodiphosphine, $P_2D_4$, has a vapour pressure which also satisfies this equation at least in the temperature range 195–240°K. The extrapolated boiling point of diphosphine is 63·5°C., Trouton's constant is 20·46, and the heat of vaporization is 6889 g.-cal./mole.[23]

The nuclear magnetic resonance spectrum of diphosphine is consistent with relatively rapid interconversion between two skew forms of the molecule. The similarity of the $J_{PH}$ coupling constants in $PH_3$ and $P_2H_4$ suggests that there is probably no great difference in bond hybridization and length between the two molecules.[185] The Raman spectrum of tetradeuterodiphosphine, $P_2D_4$, has been recorded.[186]

The specific heat of phosphonium iodide increases steadily in the temperature range $-180$ to $+10$°C. from 11·97 to 24·86 g.-cal./degree/mole.[62] Measurement of the low temperature density and coefficient of expansion has given the molar volume of phosphonium iodide as 55·9 c.c. at 0°K.[63] The magnetic susceptibilities of phosphonium bromide and phosphonium iodide are $-53{\cdot}0\times10^{-6}$ and $-71{\cdot}5\times10^{-6}$ c.g.s. units respectively at 15°C.[64] Measurement of the magnetic moment of solid phosphonium iodide has been used to demonstrate the variation of Overhauser effect with temperature.[65] The Raman spectrum of phosphonium iodide shows two intense lines consistent with its tetrahedral structure.[187]

## DISSOCIATION OF PHOSPHINE

An attempt[38] to synthesize phosphine by passing phosphorus vapour and hydrogen through a heated tube did not achieve the equilibrium previously reported for the decomposition of phosphine under similar conditions. This equilibrium was shown to be affected by the phosphine streaming rate. The decomposition of phosphine and deuterophosphine on hot wires has been studied.[66–7] The decomposition of phosphine on molybdenum at 500°C. is unimolecular at 0·01–0·1 mm. Hg pressure and tends to zero order at increased pressure up to 300 mm. Hg. At 500°C. the decomposition of phosphine on tungsten is practically independent of pressure. At 800–970°K. the decomposition of phosphine and deuterophosphine on tungsten is of first order at the lowest pressure of $1\times10^{-3}$ mm. Hg. The energy difference for $PH_3$ and $PD_3$ is 550 g.-cal. The equilibrium constants $K_I = p_{P_4}^{1/4}\cdot p_{H_2}^{3/2}/p_{PH_3}$ for the dissociation $PH_3 \rightarrow \frac{1}{4}P_{4(vap.)} + \frac{3}{2}H_2$, and $K_{II} = p_{H_2}^{3/2}/p_{PH_3}$ for the dissociation $PH_3 \rightarrow \frac{1}{4}P_{4(solid)} + \frac{3}{2}H_2$, are given by the equations[216]

$$\log K_{II} = 387/T + 0{\cdot}272 \log T + 1{\cdot}32\times10^{-3}T$$

and

$$\log K_I = -275/T + 2{\cdot}46 \log T - 4{\cdot}0\times10^{-4}T - 3{\cdot}74 \ (300\text{–}1300°)$$

The mercury-photosensitized exchange reaction between deuterium and gaseous phosphine has been investigated[68] in the temperature range 20–600°C. at pressures of 100–500 mm. Hg. The activation energy for the reaction $D + PH_3 \rightarrow PH_2D + H$ is 14·4 kcal. and for the reaction $H + PD_3 \rightarrow PD_2H + D$ is 15·0 kcal. The equilibrium constant for the reaction $PH_3 + HD \rightleftharpoons PH_2D + H_2$ calculated from spectroscopic data varies from 1·37 at 0°C. to 1·05 at 700°C. The photochemical decomposition of phosphine requires collision of a phosphine molecule with an excited metal atom to give H and probably $PH_2$ as the first step. Recombination of these products by a wall reaction is indicated.[69–71] The effect of added gases has been studied and is consistent with the above postulation. The $PH_2$ radical has been detected in the products of the photochemical dissociation of phosphine.[214] Flash photolysis of phosphine gives hydrogen and red phosphorus, probably by way of $PH_2$ and $P_2$ radicals.[192, 213] The photochemical dissociation of trideuterophosphine gives a slightly greater quantum yield than is obtained for phosphine,[72] the difference being attributed to differing secondary reaction efficiencies.

## ACID–BASE CHARACTER AND SOLUBILITY

Phosphine dissolves in water to yield a neutral solution.[73] The effect of acids and bases on this solubility is small and does not differ enough from the effect of dissolved neutral salts to be ascribed to acidic or basic properties of phosphine. The ratio of the concentration of solute in the solution phase to the concentration of solute in the gas phase has the mean value 0·201 ± 0·005 for a solution of phosphine in water at 297·5°K., Henry's law being obeyed below 1 atm. pressure. The variation with temperature of the solubility of phosphine in water is shown in Fig. 1, and the derived enthalpy of solution is $-2950 \pm 100$ g.-cal./mole. The solubility of phosphine in organic solvents is shown in Tables I and II and is much greater than in water.[9, 74, 193] The solubilities shown in Table I were obtained[9, 74] directly by allowing an excess of phosphine to come to equilibrium with the solvent in a closed system at substantially atmospheric pressure. Those shown in Table II were obtained[193] indirectly by gas–liquid distributive chromatography. The enthalpy of solution of phosphine in toluene

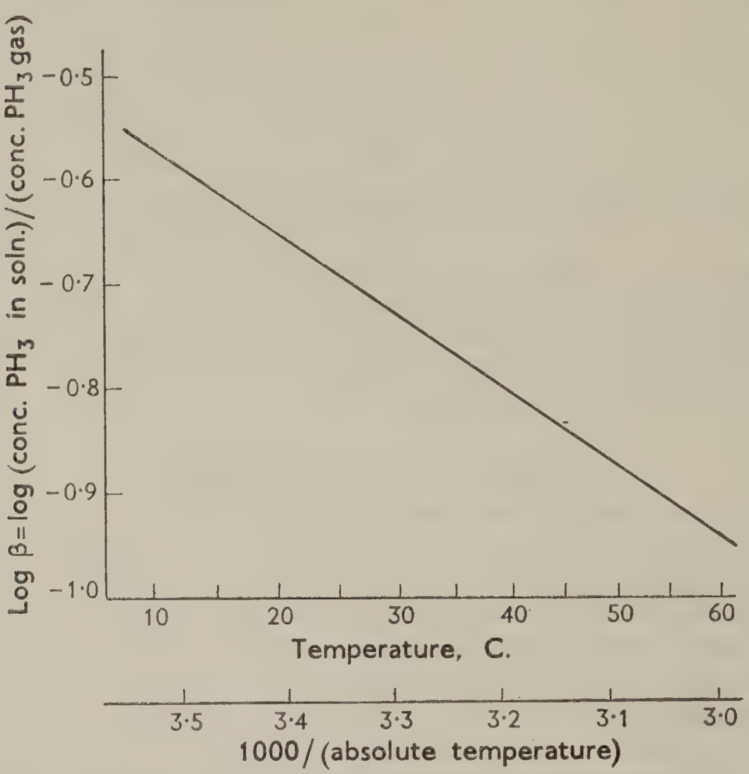


FIG. 1.—Solubility of phosphine in water, where β is the Ostwald solubility coefficient

*Table I.—Solubility of Phosphine in Organic Solvents*

| Solvent[9] | Temperature °C. | Solubility (ml. per ml. of solvent) |
|---|---|---|
| Acetone | 22·4 | 4·45 |
| Acetic acid | 20·0 | 3·19 |
| 1,2-Ethanediol | 19·2 | 1·45 |
| Propylene oxide | 22·8 | 3·06 |
| 1,2-Dichloroethane | 21·3 | 5·48 |
| 1-Nitropropane | 21·3 | 4·26 |
| Nitrobenzene | 22·5 | 3·06 |
| Aniline | 22·0 | 2·80 |
| Carbon disulphide | 21·0 | 10·25 |
| Carbon tetrachloride | 20·5 | 4·19 |
| *n*-Pentane | 21·5 | 4·33 |
| *n*-Decane | 20·9 | 5·73 |
| Benzene | 22·0 | 7·26 |
| Toluene | 22·0 | 7·15 |
| *cyclo*Hexane | 18·5 | 7·47 |
| Trifluoroacetic acid[74] | 26·0 | 15·9 |

is −3760 g.-cal./mole over the temperature range 20–40°C.,[9] and varies from −950 to −6000 g.-cal./mole over the temperature range 5–50°C. for other solvents.[193] The solubility is expressed as the volume of phosphine (measured at the temperature of the experiment and at 1 atm. pressure) dissolved in one volume of solvent under a phosphine partial pressure of 1 atm.

*Table II.—Solubility of Phosphine in Organic Solvents*

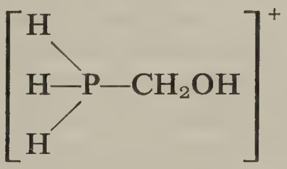
| Solvent | Distribution constant at 20°C. | Heat of solution over range 5–50°C. g.-cal./mole | Activity coefficient at −3·5°C. |
|---|---|---|---|
| Nitrobenzene | 8·59 | −1560 | 0·345 |
| Liquid paraffin | 15·9 | −3000 | 0·312 |
| Furfural | 11·8 | −3400 | 0·263 |
| 2′,2′-dichlorodiethyl ether | 20·0 | −2200 | 0·135 |
| Ethyl cellosolve | 9·4 | −950 | 0·205 |
| Didecyl phthalate | 23·5 | −4000 | 0·171 |
| Triethoxysilane | 12·2 | −5400 | 0·240 |
| Tetraethoxysilane | 12·45 | −5000 | 0·210 |
| Silicone 702-DF | 15·3 | −3600 | 0·807 |
| PFMS-4F | 16·5 | −2300 | 0·316 |
| VKZh-94B | 25·3 | —6000 | 0·208 |

The distribution constant is expressed as the volume of phosphine, measured at the partial pressure of the phosphine, dissolved in one volume of solvent.

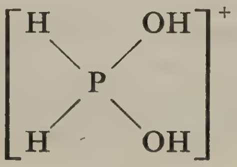
The equilibrium constant for the exchange $PH_2D(g) + H_2O(g) \rightleftharpoons PH_3(g) + HDO(g)$ using measured equilibrium data for the exchange

$$PH_2D(g) + H_2O(l) \rightleftharpoons PH_3(g) + HDO(l)^{75}$$

is calculated to be 1·52 at 25°C. No direct measurement of the acid–base strength of phosphine has been reported. The acidic and basic dissociation constants have been estimated[76] from kinetic data obtained by measuring the rate of approach to equilibrium in the hydrogen exchange between phosphine and water. Estimated values for the acid and base dissociation constants for phosphine in water are $1{\cdot}6 \times 10^{-29}$ and $4 \times 10^{-28}$, respectively. Despite the extremely small dissociation constants, proton transfers account very well for the chemical characteristics of the phosphorus–hydrogen bond.[77] It is suggested that the acid catalyzed reaction of phosphine with formaldehyde in aqueous solution proceeds via the quasi-phosphonium ion



This reaction is also reported to be subject to general metal catalysis.[78] Quasi-phosphonium ions have often been suggested as intermediates in reactions of phosphorus compounds; a sound basis for such proposals arises from a study of the tautomeric equilibrium in hypophosphorous acid[79] which proceeds via the cation



The proton affinities, or energies of the reaction $PH_4^+ \rightarrow PH_3 + H^+$ calculated from Born–Haber cycles, for phosphonium iodide, phosphonium bromide and phosphonium chloride are $-200 \pm 10$, $-209 \pm 21$ and $-217 \pm 22$ kcal., respectively.[80] A later determination gives molar lattice energies of 147·3 ± 5, and 141·2 kcal., respectively, for $PH_4Br$ and $PH_4I$, leading to a mean value of 194·5 ± 5 kcal./mole for the absolute proton affinity of phosphine.[229]

Phosphine dissolves in liquid hydrogen chloride giving phosphonium chloride which is sparingly soluble in the medium. The saturated solution has a moderate conductivity, and can be titrated with boron trichloride or boron trifluoride to give solid tetrahaloborates. Phosphonium tetrachloroborate, $PH_4BCl_4$, is similar to phosphonium iodide in stability, while the chlorotrifluoroborate, $PH_4BF_3Cl$, is somewhat less stable.[194] Phosphonium tetrabromoborate, $PH_4BBr_4$, can similarly be formed by treating a suspension of phosphonium bromide in liquid hydrogen bromide with boron tribromide.[195]

Measurements of the electrical conductivity of liquid ammonia solutions of phosphine and the solid phosphorus hydride, $P_{12}H_6$, indicate formation of salt-like compounds between ammonia and the hydrides.[81] On electrolysis of a solution of phosphine in liquid ammonia, phosphorus is deposited on the anode, apparently by discharge of the $P^{3-}$ ion.[17] The anode reaction $6PH_2^- + 2NH_3 = N_2 + 6PH_3 + 6e^-$ applies to the electrolysis of sodiophosphine and potassiophosphine in liquid ammonia,[17] but a more complicated series of reactions occurs in the similar electrolysis of tetrasodium diphosphide, protons liberated during solvent oxidation in the primary anode reaction becoming available to form the species $P_2H^{3-2-}$, $P_2H_2^{--}$ and $P_2H_3^-$ on reaction with the protophilic diphosphide ion. The ion $PH_2^-$ is proposed as an intermediate in the reaction of phosphine with methyl chloride in liquid ammonia to yield methylphosphines.[82]

The organic phosphines exhibit increasing basic properties with increasing degree of substitution. The relative basicities of phosphine and methylphosphines have been compared[83] and the basic strengths of many tertiary phosphines determined.[84] The rate of addition of alkyl halides to tertiary phosphines to give quaternary phosphonium halides is roughly correlated with the basicity of the phosphines in water.[84] Measurement of the dissociation constants of some tertiary phosphine oxides indicates that the oxides do not possess basic character.[85]

## ADDITION PRODUCTS

Phosphine forms addition compounds with a number of salts in which bonding presumably derives from donation of the unshared pair of electrons on the phosphorus atom. *X*-Ray measurements have shown that such sharing does occur in the case of the addition compound $(CH_3)_3P,AuBr_3$.[86] Diborane, $B_2H_6$, in the gas phase above −30°C., or preferably in the liquid phase above −110°C., reacts readily with phosphine to form diborane diphosphine, $B_2H_6,2PH_3$.[87] A kinetic study[88] of the homogeneous gas phase reaction of diborane with phosphine at 0°C. to yield the solid product $BH_3,PH_3$ gave observations consistent with the rate-controlling reaction $B_2H_6 + PH_3 \rightarrow BH_3,PH_3 + BH_3$ which has an activation energy of 11·4 kcal./mole. An inconclusive attempt has been made to verify this mechanism by comparison of $\Delta H$ for the reaction with postulated limits of $\Delta H$.[89] Diborane diphosphine is rapidly decomposed by water with the formation of hydrogen, phosphine and boric acid. A solution of diborane diphosphine in liquid ammonia evolves phosphine at −60°C. and yields a white solid of approximate composition $B_2H_6,PH_3,NH_3$. The compounds $B_2H_4Cl_2,2PH_3$, $B_2H_2Cl_4,2PH_3$ and $BCl_3,PH_3$, have been obtained by the reaction of diborane diphosphine with hydrogen chloride.[87] Boron trichloride phosphine is not completely dissociated in the gas phase at room temperature. It has a dipole moment of 5·2 ± 0·1 D. in benzene solution.[196] Diboron tetrachloride and phosphine at −78·5° form $B_2Cl_4,2PH_3$, a white solid which has a vapour pressure of 0·7 mm. at 25°C. and decomposes to give phosphonium chloride at 65°.[197]

Boron trifluoride and phosphine react at −130°C. to give the product $BF_3,PH_3$.[90] There is also evidence for the existence of the complex $2BF_3,PH_3$.[91]

Aluminium chloride and aluminium bromide react with phosphine at 70°C. and aluminium iodide reacts at 120–130°C. to form the white crystalline compounds $AlCl_3,PH_3$, m.p. 81–83°C., $AlBr_3,PH_3$, m.p. 114–118°C. and $AlI_3,PH_3$, m.p. 148–150°C., which can be readily fused and sublimed.[92] The chloride complex combines exothermically with alkyl halides to give primary alkyl phosphines.[198] Similar compounds with phosphine were not obtained in the case of beryllium halides.[92] The reaction of phosphine with other metal halides[93–4] yields $2SnCl_4,3PH_3$, $TiCl_4,2PH_3$, $TiCl_4,PH_3$, $TiBr_4,2PH_3$, $TiBr_4,PH_3$, $CuCl,2PH_3$, $CuCl,PH_3$, $CuBr,2PH_3$, $CuBr,PH_3$, $CuI,2PH_3$, $CuI,PH_3$, $AgI,PH_3$, $2AgI,PH_3$ and the very unstable product $AuI,PH_3$. The other silver and gold halides, tin tetraiodide, titanium tetraiodide and zirconium chloride do not react with phosphine. The heats of formation of some metal halide phosphines have been calculated from vapour pressure data[94] and measured calorimetrically[95]; these range from 8·6 to 16·0 kcal./mole of gaseous phosphine added to the solid metal halide. Copper halide phosphines have also been prepared by the reaction of phosphine and the copper halide in alcoholic solution.[96] The copper halide phosphines are soluble in ethanol, diethyl ether, acetone, chloroform, carbon tetrachloride and benzene.[96] Both carbon tetrachloride and silicon tetrachloride are soluble in liquid phosphine.[93]

Diphosphine reacts with boron trifluoride giving a product $P_2H_4,2BF_3$ which is fairly stable below −118°, but rapidly evolves phosphine at higher temperatures. Diborane and diphosphine yield a white solid, $P_2H_4,B_2H_6$, which is stable at −78°. It melts with little decomposition at −40°, but at room temperature evolves $B_2H_6$, $PH_3$ and $H_2$, leaving a non-stoicheiometric solid containing boron, phosphorus and hydrogen.[199]

It has been proposed[97, 25] that solid hydrogen phosphide, $P_{12}H_6$, is a sorption compound of phosphine and amorphous phosphorus. Theoretical consideration[98] of the structure of inert gas hydrates indicates that the formula of the solid phosphine hydrate should be $PH_3,5{\cdot}9H_2O$, the water occupying voids between the phosphine molecules.

The organic derivatives of phosphine form addition compounds which are similar to those formed by phosphine itself. Some of these compounds have proved of considerable interest. For example, mixtures of dimethylphosphine and trimethylaluminium react at temperatures above 215°C. to form methane and a solid trimeric product having formula $[(CH_3)_2P.Al(CH_3)_2]_3$ which probably has a six-membered ring structure of alternating phosphorus and aluminium atoms.[99] The extremely stable trimeric product having formula $[(CH_3)_2P.BH_2]_3$ is obtained when the addition compound formed between dimethylphosphine and borine is heated at 150°C.[100] This trimer also probably has a six-membered ring structure of alternating phosphorus and boron atoms. An extensive chemistry of organic compounds exhibiting phosphorus–boron bonding has been developed. Tertiary phosphines have been purified by distillation of carbon disulphide from their carbon disulphide adduct, for example $(CH_3)_3P,CS_2$.[101] Complex co-ordination compounds are formed between tertiary phosphines and platinum salts,[102–5] palladium salts,[105–6] nickel salts[107] and aqueous silver ions.[108] *Cis* and *trans* isomers have been obtained for the addition compounds based upon platinum.[102, 109] Compounds have been prepared in which tertiary phosphines partly replace the carbonyl group in iron,[110–11] ruthenium[112] and rhodium[112] carbonyl halides.

Unlike the phosphorus halides, phosphine does not form an addition compound with osmium tetroxide, $OsO_4$.[113]

## OXIDATION OF PHOSPHINE

The reaction of phosphine with oxygen has been widely studied and shown to involve a branching chain reaction. At ordinary temperatures a phosphine–oxygen mixture reacts explosively between two sharply defined pressure limits which depend on the composition of the mixture. The lower explosion limit is diminished by ultraviolet radiation owing to the formation of an active substance from the phosphine[114] or to a surface effect.[70–1] The lower explosion limit is also diminished by the presence of inert gases[115–7] which impede chain diffusion to the walls of the containing vessel. The inhibition is lost when the pressure of the inert gas reaches the same order of magnitude as that of the phosphine and oxygen. As the temperature is raised the lower explosion pressure limit falls and the upper limit rises.[118] At and above the upper limiting pressure oxygen is an inhibitor.[119–20] The upper limit of partial pressure of oxygen is proportional to the square root of the partial pressure of phosphine.[121] At high pressures the chain reaction is not affected by the walls of the containing vessel, but deactivation occurs when an activated species strikes both an oxygen molecule and a third body.[122] The upper and lower explosion limits of trideuterophosphine coincide with those of phosphine, the chain lengths are identical, and the individual steps in the oxidation of deuterophosphine and phosphine have similar rates.[72] At pressures below the lower explosion limit the reaction between phosphine and oxygen is immeasurably slow. Reaction at low pressure is induced by ignition in the presence of tungsten and molybdenum filaments and occurs almost wholly on the surface of the metal.[123] Mixtures of phosphine and oxygen ignite by dilatation[124] with instantaneous reaction if the gases are very dry. The ignition pressure rises sharply with increasing temperature and increases with increased phosphine partial pressure. The ignition pressure falls with increasing water content of the gases and falls very slightly in the presence of inert gases. Methylphosphine, $CH_3PH_2$, depresses the ignition pressure and does not itself ignite with oxygen on dilatation.[124] The rôle of the hydroxyl radical in the mechanism of combustion of phosphine and other hydrogen-containing compounds has been discussed.[125] Results of the flash photolysis of mixtures of phosphine and oxygen above the upper, and below the lower, explosion limits are consistent with a mechanism in which OH and $PH_2$ radicals carry on the straight chains, while O atoms are involved in branching only.[200]

The selective oxidation of phosphine in admixture with other oxidizable gases, for example gases obtained from the reaction of phosphorus with steam, has received some attention. Suitable oxidants include oxygen,[126] oxygen with nitric acid[127–8] and $NO+NO_2$ as catalyst,[129] aqueous phosphoric acid-containing ozone,[130] steam[131–2] in the presence of metal catalysts, sulphuric acid[133] with catalysts, sulphur dioxide[8] and anodic oxidation in phosphoric acid electrolyte.[134] A study has been made of the catalytic oxidation of phosphine adsorbed on active carbon[135–8] and of the phosphine-induced oxidation of carbon monoxide.[139–40]

Hypophosphorous acid is formed by the oxidation of phosphine in an aqueous suspension of iodine.[141]

## OTHER REACTIONS

Neutron bombardment of phosphine yields radiophosphine, hydrogen and phosphorus.[142] No evidence of higher hydride formation was detected in experiments in which phosphine was brought into contact with atomic hydrogen.[143–4] The main products of the reaction between phosphine and active nitrogen are molecular hydrogen and α-polyphosphorus nitride, $(PN)_n$.[145] Phosphine reacts with heated uranium,[146–7] uranium hydride,[148] thorium[149] and thorium hydride[150] to form the metal phosphide. It reacts with heated sulphur to give gaseous hydrogen sulphide and a residue comprising a mixture of phosphorus sulphides.[151] Phosphine reacts with hydrogen sulphide much more slowly than with sulphur, the reaction proceeding significantly only at temperatures above 320°C. to produce hydrogen and ill-defined phosphorus sulphides.[151] The reaction of phosphine with sulphur dichloride, $SCl_2$, gives a yellow viscous liquid of composition approximating to $H_2ClPS$. Trifluoromethylsulphenyl chloride, on the other hand, has yielded bis(trifluoromethyl)phosphine, $(CF_3S)_2PH$ (v.p. 149 mm. at 40°) and tris(trifluoromethyl)phosphine, $(CF_3S)_3P$. The latter is a colourless liquid, f.p. $-75°$, v.p. 30·5 mm. at 20°, and it decomposes above 50°.[201]

Pure sodiophosphine, $NaPH_2$, can be prepared by causing phosphine to react with a liquid ammonia solution of triphenylmethyl sodium.[152] Lithiophosphine, $LiPH_2$, is obtained almost quantitatively from the reaction of phosphine with phenyl lithium.[153] Both are colourless solids, which ammonolyze slowly in contact with liquid ammonia. Potassiophosphine, $KPH_2$, can, however, be prepared as a white, spontaneously inflammable solid, by direct interaction of phosphine with a solution of potassium in liquid ammonia, and shows little tendency to ammonolysis even during several days at $-33°$.[232–3] Phosphine reacts with ethyl magnesium bromide to give $PH_2MgBr$[152] or $PH(MgBr)_2$.[154] Trimethyl indium reacts with boiling liquid phosphine to give the complex $Me_3In,PH_3$. This decomposes at $-78°$ evolving $PH_3$ and $Me_3In$, and leaving a residue $(MeInPH)_x$, which further decomposes violently to methane and indium phosphide at 270° to 300°.[202] Gallium oxide is reduced by phosphine to gallium phosphide in high yield at 950°C.[203] Phosphine reacts with lithium aluminium hydride in diethyleneglycol dimethyl ether, yielding unstable $LiAl(PH_2)_4$. No reaction occurred in the absence of solvent.[204]

The partially substituted metal phosphine derivatives have found application as intermediates in organo-phosphorus chemistry.[205] The reaction of phosphine with solutions of nickel salts to give nickel phosphides and ill-defined alloys has been studied in various solvents.[155] The formation of $P(HgCl_2)_3$ by reaction between phosphine and aqueous mercuric chloride solution has been applied analytically.[156, 228] The pyrolysis of silane, $SiH_4$, with phosphine has been reviewed.[157] The complex mixture of silylphosphines and silanes includes monosilylphosphine, $PH_2SiH_3$, a colourless liquid b.p. 12·7°C.[206–7] decomposed by acid, alkali, ammonia or alcohol, with the formation of phosphine.[208] Trisilylphosphine, $P(SiH_3)_3$, is obtained by the reaction of silyl bromide and potassiophosphine:

$$3SiH_3Br + 3KPH_2 \rightarrow P(SiH_3)_3 + 2PH_3 + 3KBr$$

It is a colourless liquid, spontaneously inflammable in air, and has a vapour pressure given by $\log p = -(1901{\cdot}9/T + 7{\cdot}792)$ over the range $-30°$ to 11°C.[209]

With aliphatic aldehydes phosphine may form α-hydroxyalkylphosphines or phosphonium salts, 1,3-dioxa-5-phospha*cyclo*hexane derivatives, or spirophosphonium salts.[210] In strong acid media ketones give primary and secondary phosphine oxides.[211] Phosphine reduces aromatic nitrocompounds to azoxy derivatives in high yields, and converts sulphonyl chlorides, $RSO_2Cl$, to the corresponding mercaptans RSH, disulphides RSSR and phosphorotrithioates $(RS)_3PO$.[212]

That diphosphine is less reactive than phosphine is ascribed to a general observation that repetition of a function within a molecule causes lowered reactivity of the molecule.[158]

The acid hydrolysis of mixed phosphides, arsenides, nitrides and germanides of calcium and magnesium gives the following products, detected by mass spectroscopy[215]:

$Mg_3P_2/Mg_3As_2$: $P_3H_5$, $As_3H_5$ and $PH_2AsH_2$
$Mg_3P_2/Mg_3N_2$: $P_3H_5$, $PH_2NH_2$, $PH(NH_2)_2$, $P(NH_2)_3$ and $P_2H_3NH_2$
$CaGe/Ca_3P_2$: $P_3H_5$ and $GeH_3PH_2$

Trigermylphosphine, $(GeH_3)_3P$, prepared by treating trisilylphosphine with a small excess of germanyl bromide at room temperature, is a colourless liquid, m.p. $-83{\cdot}8°$, v.p. at 0° ~ 1 mm., which decomposes slowly at room temperature and rapidly at 55°. The infra-red and Raman spectra suggest strongly that the molecule is not planar.[217] The action of the electrodeless discharge on gaseous equimolecular mixtures of $PH_3 + H_2S$ or $PD_3 + H_2S$ at 0·1 torr, gives the compounds $H_2PSH$ or $D_2PSD$, identified by their mass spectra, and decomposing above $-130°$ to an amorphous involatile yellow residue. Their infra-red spectrum shows a sharp absorption at 477 cm.$^{-1}$, identified with the P–S single bond.[223]

**Refs. p. 284**

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## SECTION VII

# THE METAL PHOSPHIDES

### BY A. WILSON

The early literature is well reviewed by Mellor[1] and Gmelin.[2] In more recent work, methods of preparation, heats of formation, and methods of determination have been collected together for transition metal phosphides,[3] whilst melting points and a few thermochemical data have been included in a review dealing with phosphides as well as other classes of compounds.[4] Unit cell dimensions and magnetic susceptibilities have been given for a series of rare earth phosphides[547] whilst densities, oxidation resistances, decomposition temperatures, hardnesses and specific resistivities have been given for some transition-metal phosphides.[566] A valuable summary of crystal data, densities and thermal data for fifty-two metallic phosphides appeared in a report by the Tennessee Valley Authority,[5] but the most comprehensive collections of data on phosphides and their chemistry have been made by Hansen,[6] whose emphasis is on phase diagram work, by Samsonov and Vereikina,[7] by Aronsson, Lundström and Rundqvist[689] and by Van Wazer.[8]

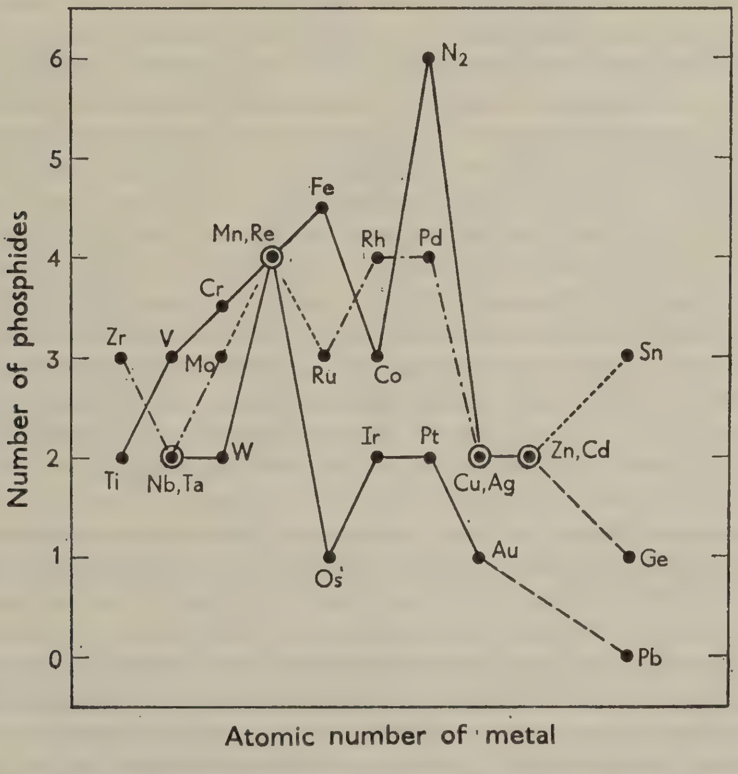

FIG. 1.—Periodic frequency of phosphides

Methods of preparation of phosphides will be discussed under the different metals concerned but two methods which have been used most successfully are the 'Faraday Method' and electrolysis of fused salts.[9–10] The 'Faraday Method' consists essentially of heating the metal with excess of red phosphorus at high temperatures in an inert atmosphere or in an evacuated sealed tube, whilst the fused-salts method consists in electrolyzing molten alkali-metal phosphates to which appropriate metal oxides or halogen salts have been added. Variations in current, voltage and bath composition give different phosphides. High melting binary phosphides, such as zinc or sodium phosphide, can be made below their melting points from the elements if the metal is reduced to particles small enough to react completely.[583]

A statistical study of the number of stable phosphides formed by different metals has been made, the results for which are summarized in Fig. 1.[11]

A survey of compounds of type XY and $X_2Y$ where Y can be phosphorus has confirmed the assumption that, in general, the densities of stable phosphides are arithmetic means of the densities of the separate components.[12]

Fuller structural information on phosphides is to be found in Section XXXIV, whilst relevant vapour pressure data are given in Section V. Where $\Delta H$ values are given a negative sign indicates a heat loss for the system.

## GROUP 1A

### Lithium

After unsuccessful attempts to prepare trilithium monophosphide by causing lithium to react with phosphorus in liquid ammonia, a material approaching the composition of trilithium monophosphide was eventually obtained by heating together the correct quantities of lithium and phosphorus in a closed vessel.[13] The compound has also been obtained by reacting lithium monophosphide with excess of lithium[14] and by the rather unusual method of treating phenyl lithium in ether with phosphine. The mixture was refluxed, filtered, and washed with ether to give as product trilithium monophosphide.[15] This is a grey compound, having *d* 1·4 g./c.c. and a crystal structure of the sodium arsenide type.[13] The estimated heat of formation is −44 kcal./mole.[16] Trilithium monophosphide is insoluble in dioxan, benzene, ether, tetrahydrofuran and light petroleum, and is sensitive to air and moisture.[15]

The reaction of lithium and phosphorus in liquid ammonia has been used by other workers[17] to obtain a compound with the empirical formula $Li_2P$. It is considered that under such conditions normal phosphides are not obtained and that the product is probably dimeric. In another investigation a residue corresponding closely to $Li_2P$ was obtained when $(PH)_x$ containing lithium hydride was heated slowly to 300°C.[18] Dilithium phosphide, or the product obtained from the synthesis in ammonia, is soluble in liquid ammonia forming a yellow–orange solution which conducts electricity.[17] It has been estimated that the heat of formation is zero.[16]

Lithium monophosphide has been prepared by three different routes although two of them are somewhat similar.[14] In one method lithium metal was added to molten white phosphorus and the excess of phosphorus distilled off under vacuum at 280°C. In the second method lithium was treated with phosphorus vapour below 400°C., whilst in the third method it was obtained by causing lithium hydride to react with red phosphorus at 500°C.[14] The heat of formation has been estimated to be 34 kcal./mole.[16] It is rather a reactive compound and is sensitive to air or moisture. With water a reaction proceeds readily which produces a yellow precipitate identified as $(PH)_x$. If it is heated in a vacuum, decomposition with the formation of phosphorus takes place at 600°C. Other phosphides such as the trilithium phosphide can be prepared from it and at temperatures about 900°C. it reacts with ammonia to form a compound $LiPN_2$.[14]

If phosphine is passed into a solution of lithium in liquid ammonia at −80°C., the blue solution turns yellow and a white crystalline powder, $PH_2Li,4NH_3$, can be recovered.[19] When heated this compound gives a substance with the empirical formula $Li_2PH$.[20] These compounds are probably not true phosphides since other workers have adapted the reaction to the preparation of monosodium phosphine.[21]

Several ternary compounds of lithium with another metal and phosphorus have been reported.[22–9] The compounds lithium magnesium phosphide and lithium zinc phosphide have been prepared by heating the elements together in a bomb in the absence of air.[28] Other ternary compounds, $Li_7VP_4$, $Li_5SiP_3$, $Li_5GeP_3$, $Li_5TiP_3$, $Li_3GaP_2$, $Li_3AlP_2$ and a series represented by the formula $Li_{8-x}Mn_xP_4$ have been made by heating finely ground mixtures of lithium phosphide, metal and phosphorus in bombs at temperatures varying between 500° and 1000°C. Variations of this method have also been successfully employed, ternary compounds being obtained by heating together lithium, metal and phosphorus, or by heating together trilithium phosphide and metal phosphide.[22] An attempt to produce $Li_9CrP_5$ was unsuccessful but by heating together trilithium phosphide, chromium, red phosphorus and sulphur at 800°C., it was possible to prepare mixed crystals of $Li_9CrP_5$ and $Li_2S$. *X*-Ray methods were used to differentiate between the products of these reactions and the reactants.[27] A ternary compound in which the third element was not a metal was prepared by causing trilithium phosphide to react with ammonia at 950°C. and more readily by heating lithium amide with phosphonitrilimide.[14] The last reaction is represented thus:

$$(1) \qquad LiNH_2 + HNPN \xrightarrow{600°C.} LiPN_2 + NH_3$$

In the series $Li_{8-x}Mn_xP_4$ the cubic compound $Li_7MnP_4$ forms a mixed crystal series extending as far as the composition $Li_{6 \cdot 67}Mn_{1 \cdot 33}P_4$. This composition is the beginning of a second mixed series which extends as far as $Li_{5 \cdot 5}Mn_{2 \cdot 5}P_4$.[29] Table I and Table II show some properties and preparation conditions of lithium phosphides.

*Table I.—Data on Some Mixed Phosphides containing Lithium*

| Compound | Colour | Molecular volume (c.c.) | Unit cell constants (kx units) | Ref. |
|---|---|---|---|---|
| LiMgP | brown | 32·6 | 6·01 | 28, 30 |
| LiZnP | brown | 28·8 | 5·77 | 28, 30 |
| $Li_3AlP_2$ | yellow-brown | 58·4 | $a = 11{\cdot}47$, $b = 11{\cdot}61$, $c = 11{\cdot}73$ | 24 |
| $Li_3GaP_2$ | medium brown | 58·0 | 11·74 | 24 |
| $Li_5SiP_3$ | brown | 90·0 | 5·84 | 24 |
| $Li_5GeP_3$ | brown | 91·7 | 5·88 | 24 |
| $Li_5TiP_3$ | brown | 95·4 | 5·96 | 24 |
| $Li_7VP_4$ | brown | | 5·98 | 27 |
| $Li_9CrP_5$ | | | 6·01* | 27 |

* An extrapolated value from data on $Li_9CrP_5$–$Li_2S$ mixed crystals.

Semiconductor properties have been predicted for lithium magnesium phosphide and lithium zinc phosphide.[31] Trilithium aluminium diphosphide has m.p. over 700°C. and a specific resistance greater than $10^8$ ohms cm. at room temperature.[22] It is thought that all of the phosphides listed in Table I have ionic character and they all react rapidly with water or acids to liberate phosphine.[22] This is also true of the grey to black phosphides which are listed in Table II. The water sensitivity of these decreases with increasing manganese content.[29] The compound lithium dinitrogen phosphide appears to be different from the other ternary phosphides. *X*-Ray analysis shows that its crystal structure is body centred tetragonal with lithium atoms lying in tetrahedral holes in a framework of $PN_4$ tetrahedra. The $[PN_{4/2}]'$ group is isoelectronic with $SiO_{4/2}$ which suggests that the compound may be similar to silicates. Other properties are not at variance with this suggestion since lithium dinitrogen phosphide is colourless, stable under vacuum to 1000°C., decomposes without melting at high temperatures, is stable to acids and bases and dissolves slowly in concentrated sulphuric acid.[14]

*Table II.—Lithium–Manganese–Phosphide Preparations with Conditions of Preparation and Unit Cell Constants*

| Preparation | $n$* | Preparation conditions | | Cell constants | | $c/a$ | Volume of the unit cell A.$^3$ |
|---|---|---|---|---|---|---|---|
| | | hr. | °C. | $a$ A. | $c$ A. | | |
| $Li_{7\cdot33}Mn_{0\cdot67}P_4$ | 7·00 | 4 | 850 | 5·977 | | | 213·5 |
| $Li_{7\cdot2}Mn_{0\cdot8}P_4$ | 6·00 | 4 | 850 | 5·977 | | | 213·5 |
| $Li_7MnP_4$ | 5·00 | 4 | 850 | 5·977 | | | 213·5 |
| $Li_{6\cdot8}Mn_{1\cdot2}P_4$ | 4·33 | 4 | 810 | 5·963 | | | 212·0 |
| $Li_{6\cdot67}Mn_{1\cdot33}P_4$ | 4·00 | 4 | 800 | 5·950 | | | 210·7 |
| $Li_{6\cdot6}Mn_{1\cdot4}P_4$ | 3·86 | 4 | 800 | 5·945 | | | 210·1 |
| $Li_{6\cdot5}Mn_{1\cdot5}P_4$ | 3·67 | 4 | 800 | 5·933 | 5·956 | 1·004 | 209·7 |
| $Li_{6\cdot36}Mn_{1\cdot64}P_4$ | 3·44 | 4 | 800 | 5·918 | 5·965 | 1·008 | 208·9 |
| $Li_{6\cdot2}Mn_{1\cdot8}P_4$ | 3·22 | 4 | 800 | 5·906 | 5·974 | 1·011 | 208·4 |
| $Li_6Mn_2P_4$ | 3·00 | 4 | 800 | 5·888 | 5·983 | 1·016 | 207·4 |
| $Li_{5\cdot8}Mn_{2\cdot2}P_4$ | 2·82 | 4 | 800 | 5·870 | 5·976 | 1·018 | 205·9 |
| $Li_{5\cdot5}Mn_{2\cdot5}P_4$ | 2·60 | 3 | 800 | 5·839 | 5·963 | 1·020 | 203·3 |
| $Li_5Mn_3P_4$ | 2·33 | 4 | 800 | 5·838 | 5·962 | 1·021 | 203·2 |
| $Li_4Mn_4P_4$ | 2·00 | 4 | 800 | 5·841 | 5·964 | 1·021 | 203·5 |

* Oxidation state of the manganese.

## Sodium

Sodium and phosphorus, when heated together in the correct proportions in an inert atmosphere, give the compound trisodium phosphide.[13, 32–3] It has been identified by means of *X*-ray photographs which show it to possess the sodium arsenide type of structure with $a = 4{\cdot}980$ and $c = 8{\cdot}797$ A.[13] Although the existence of this phosphide has been questioned,[8] it now seems to be established as the major product resulting from the reaction of white phosphorus with sodium dispersions in inert organic media.[584] The density, 1·74 g./c.c., has been calculated from the *X*-ray data.[13] From its heat of reaction with N-HCl, which is −149·8 kcal./mole, a heat of formation of −32·0 kcal./mole is calculated.[32] This figure compares with −40·0 kcal./mole, estimated using data for oxides as a guide[16] and a value of −28·3 kcal./mole determined by other workers.[33] This phosphide is easily hydrolyzed and the heat of reaction according to equation (2) is −93·0 kcal.[33]:

$$(2) \qquad Na_3P(s) + 3H_2O(l) \rightarrow 3NaOH(40\% \text{ aq. soln.}) + PH_3(g)$$

Trisodium phosphide has been used as a catalyst for olefin polymerization.[588]

Disodium pentaphosphide (Mellor, VIII, 835) is reported as being formed when monosodium phosphine is heated to 380°C.[20]

Reaction of sodium with phosphorus in liquid ammonia has been studied by two groups of investigators.[17, 34–7] Electrolysis of ammoniacal solutions of sodium was studied. One of the main processes taking place was explained by postulating the protonation of a diphosphide species $P_2^{4-}$.[36–7] Claims to have prepared tetrasodium diphosphide containing two molecules of ammonia of crystallization[17, 34] have been questioned by later workers[35] who state that the products of the reaction are disodium dihydrogen diphosphide and monosodium amide. Chemical analysis and *X*-ray powder photographs were used to identify these two compounds, respectively. The reaction of ammonium bromide with the ammoniacal solutions of sodium and phosphorus has been studied by both groups, one of which[34] puts forward equation (3) to represent the reaction and the other[35] equation (4):

$$(3) \qquad Na_4P_2 + 2Na + 4NH_4Br \xrightarrow[\text{ammonia}]{\text{liquid}} 2NaPH_2 + 4NaBr + 4NH_3$$

$$(4) \qquad Na_2H_2P_2 + 2NaNH_2 + 4NH_4Br + 2Na \xrightarrow[\text{ammonia}]{\text{liquid}} 2NaPH_2 + 4NaBr + 6NH_3$$

An estimate of 3 kcal./mole for the heat of formation of disodium phosphide has been made.[16]

For sodium monophosphide an estimated heat of formation is 34 kcal./mole.[16]

### Potassium

Tripotassium phosphide, formed from phosphorus vapour and potassium, has been shown to have the $Na_3As$ type of structure with $a = 5{\cdot}69$ and $c = 10{\cdot}05$ A.[38] It is green and has $d$ 1·74 g./c.c.[38] An estimated value of $-40$ kcal./mole has been reported for the heat of formation of tripotassium phosphide, while that of dipotassium phosphide is estimated as 3 kcal./mole.[16]

Potassium and phosphorus dissolve in liquid ammonia to form a compound the empirical formula of which is $K_3P_2$. It is probably dimeric and its solution in liquid ammonia conducts electricity. It reacts with lithium or sodium to form mixed phosphides.[17]

Monopotassium phosphide has an estimated heat of formation of 34 kcal./mole.[16]

A dipotassium pentaphosphide is said to be formed from $KPH_2$ when it is heated to 320°C.[20]

An *X*-ray study of $KPH_2$, which is really a substitution product of phosphine rather than a true phosphide, shows it to be monoclinic with $a = 7{\cdot}952$, $b = 4{\cdot}450$, $c = 5{\cdot}275$ A., $\beta = 120{\cdot}5°$, $\rho_{calc.} = 1{\cdot}488$ g./c.c.[39]

### Rubidium

$RbPH_2$, which is probably a substitution compound of phosphine, has been examined by *X*-ray methods and shown to be monoclinic with $a = 8{\cdot}419$, $b = 4{\cdot}746$, $c = 5{\cdot}513$ A., $\beta = 122{\cdot}0°$, $\rho_{calc.} = 2{\cdot}10$ g./c.c.[39]

### Cæsium

Alloys with phosphorus which were of unknown composition have been investigated as photoelectric materials, and found to have a sensitivity lower than fifteen microamperes per lumen.[40]

## GROUP 1B

### Copper

In copper sulphate solution white phosphorus becomes coated with a product the composition of which varies with changes in the concentration of the solution. In 0·1N. copper sulphate, for example, the material is reported as being black and having the composition $Cu_9P_{1{\cdot}6}$.[41]

Heating copper with red phosphorus in an evacuated flask for 20 hr. at 640°C. and then for a further 5 hr. at 1000°C. produces tricopper phosphide.[42] This is also produced when copper phosphates are reduced with hydrogen above 350°C.[43] Electrolytic methods, one involving the electrolysis of fused alkali metal phosphates containing copper compounds[44, 10] and the other the passage of a silent electrical discharge through compounds such as phosphorus trichloride and phosphorus tribromide using copper electrodes,[45] have also been shown to produce tricopper phosphide. A tensimetric analysis of the copper–phosphorus system, shown in Fig. 2, revealed the presence of this phosphide[46] and laboratory scale methods have been described for making copper–phosphorus alloys which contain it.[47] Tricopper phosphide is a dark grey material which melts at 1023°C.[48] and has hexagonal crystal structure, with $a = 7{\cdot}070$ and $c = 7{\cdot}135$ A.[49] Density determinations gave values of $d = 7{\cdot}147$ g./c.c.[42] and $d = 7{\cdot}09$ g./c.c.[44] The molecular volume is 31·0 c.c.[42] A heat of formation of $-32{\cdot}0$ kcal./mole was measured by combining red phosphorus and copper in a bomb at 630°C.,[50] and the free energy of formation of solid $Cu_3P$ from gaseous elements is given as $\Delta G = -47{,}400 + 11{\cdot}3T$ g.-cal./mole over the temperature range $T = 298$–1303°K.[548] Electrical measurements show that tricopper phosphide is almost a metallic conductor; its specific resistance at 0°C. is $1{\cdot}4 \times 10^{-4}$ ohms-cm. and the variation with temperature of this property is shown in Fig. 3. The magnetic

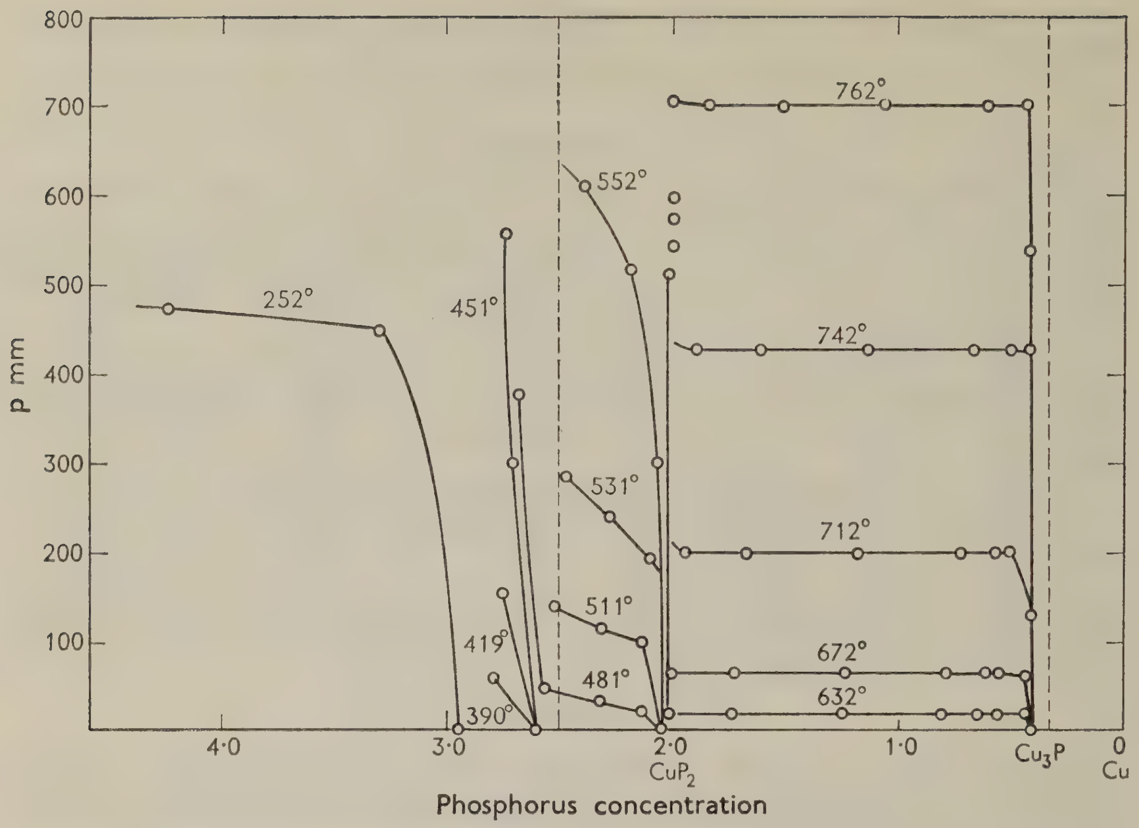

FIG. 2.—Vapour pressure–concentration diagram of the copper–phosphorus system

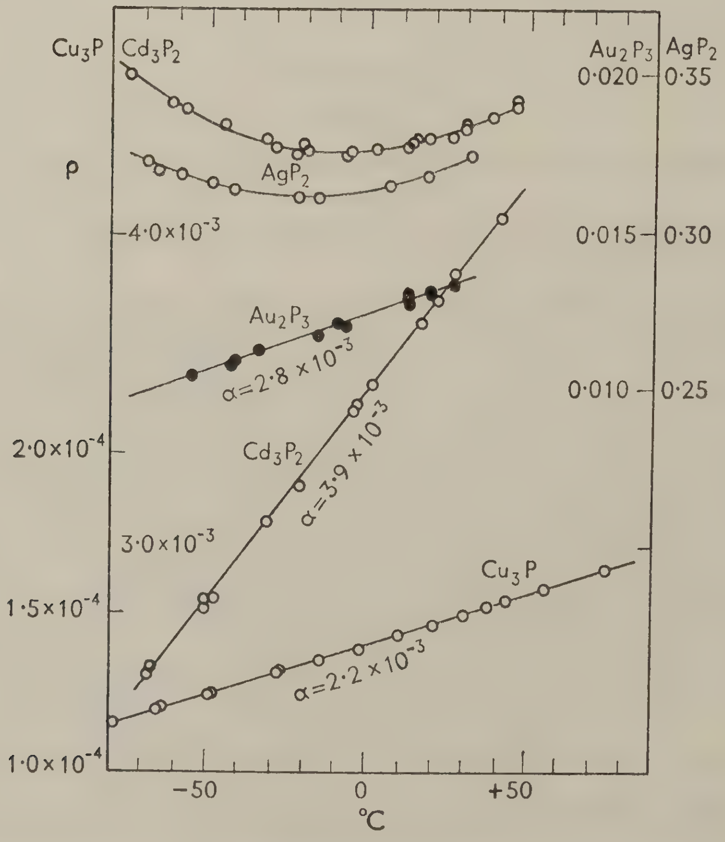

FIG. 3.—Specific resistance, $Q$, of $Cu_3P$, $Cd_3P_2$, $Au_2P_3$ and $AgP_2$ plotted against temperature. $\alpha$ is the temperature coefficient of the specific resistance

susceptibility measurements for this diamagnetic compound[51] are summarized in Table III.[42] It is oxidized by hot air and attacked by acids, feebly by dilute hydrochloric acid but more rapidly by nitric acid and hot sulphuric acid.[44]

*Table III.—Magnetic Susceptibilities of Tricopper Phosphide and Copper Diphosphide*

| | $-\chi_{gr}\cdot10^6$ | | | | | Mean | $-\chi_{mol}\cdot10^6$ | $-\chi_P\cdot10^6$ |
|---|---|---|---|---|---|---|---|---|
| $T$°C. | −183 | −78 | 20 | 168 | 388 | | | |
| $Cu_3P$ | 0·13 | 0·17 | 0·13 | 0·14 | 0·19 | 0·15 | 33 | 15 |
| $CuP_2$ | 0·25 | 0·32 | 0·29 | 0·25 | 0·30 | 0·30 | 35 | 15 |

In the above table $\chi_{gr}$, $\chi_{mol}$ and $\chi_P$ are the magnetic susceptibilities per gram of compound, per mol. of compound, and per atom of phosphorus, respectively.

The electrolysis of fused alkali-metal phosphates containing copper salts has also been used to produce dicopper phosphide,[44, 10] a dark brown compound, *d* 5·51 g./c.c.[44] It shows *p*-type semiconducting properties below 219°K.[51] and readily evolves phosphorus which ignites spontaneously.[44]

A patent has made reference to tricopper diphosphide. It is claimed that the phosphide can be prepared at 1100° to 1200°C. according to equation (5)[52]:

$$3Cu_2O+4H_3PO_4+7C \rightarrow 2Cu_3P_2+6H_2O+6CO_2+CO \qquad (5)$$

A magnetic test for superconductivity on copper monophosphide down to 1·28°K. gave negative results.[53]

In a tensimetric analysis of the copper–phosphorus system, copper diphosphide was identified.[46] It is formed at the same time as tricopper phosphide when copper phosphates are reduced by hydrogen at 350°C.[43] and can also be prepared from tricopper phosphide by heating it with the calculated quantity of phosphorus at 600°C. for 24 hr.[42] Its density is 4·20 g./c.c. and it has a molecular volume of 29·9 c.c.[42–6] Copper diphosphide has monoclinic symmetry, with $a=5{\cdot}802$, $b=4{\cdot}807$, $c=7{\cdot}525$ Å. and $\beta=112{\cdot}68°$. The space group is $P2_1/c$ with 4 copper atoms in one 4(*e*) position and 8 phosphorus atoms in two further sets of 4(*e*) positions. The melting point is approximately 900°C.[585] From dissociation pressures, the heat of dissociation, according to equation (6), is $\Delta H = +52\pm0{\cdot}8$ kcal./mole[46, 42] and the free energy of formation of solid $CuP_2$ from its gaseous elements is given by

$$\Delta G = -46{,}300+22{\cdot}5T \text{ g.-cal./mole } (T \text{ in °K.})^{548}$$

$$\tfrac{12}{5}CuP_2(s) \rightarrow \tfrac{4}{5}Cu_3P(s)+P_4(g) \qquad \bar{t} = 697°C. \qquad (6)$$

The vapour pressure variation with temperature can be represented by equation (7)[42]:

$$\log p_{(mm.)} = -11{\cdot}370\times10^3/T+13{\cdot}827 \qquad (7)$$

The specific resistance and its variation with temperature for copper diphosphide are shown in Fig. 4,[51] whilst its magnetic susceptibilities are shown in Table III.[42] The compound is similar to tricopper phosphide in its chemical properties, being oxidized by hot air and attacked by acids.[44]

Attempts to prepare copper triphosphide by heating together the calculated quantities of phosphorus and copper resulted only in the formation of a solid solution of copper in copper diphosphide.[46]

Some ternary compounds containing copper, phosphorus, and a third element have been prepared by direct combination of the elements in a silica tube heated for 2–3 days at 800°C. followed by 3–4 hr. at 1200°C.[55] Measurements on these compounds showed them to be cubic: CuPS has $a=9{\cdot}70$ Å., $d_{calc.}=5{\cdot}54$ g./c.c., $d_{obs.}=5{\cdot}30$ g./c.c. whilst CuPSe has $a=10{\cdot}15$ Å., $d_{calc.}=6{\cdot}61$ g./c.c., $d_{obs.}=6{\cdot}40$ g./c.c.[55] They are inert towards most mineral acids, though aqua regia attacks them slowly in the cold, and concentrated nitric acid attacks them on prolonged boiling. CuPSe is attacked by concentrated sulphuric acid. Warm alkali is without effect. In a sealed tube they do not melt below 1200°C. but heating under vacuum decomposes them.[55] The analogous compounds $CuPS_2$ (bright yellow powder $d_{obs.}$ 3·55, f.p. 910°C.) and $CuPSe_2$ (vitreous globules forming a black powder $d_{obs.}$ 5·01, f.p. 640°C.) have been made from the elements. Both have a wurtzite-type lattice. They are chemically inert, fairly stable in air or oxygen-free water, not attacked by mineral acids or concentrated alkalis, but dissolved by boiling concentrated nitric or sulphuric acids. They decompose on heating according to the equation

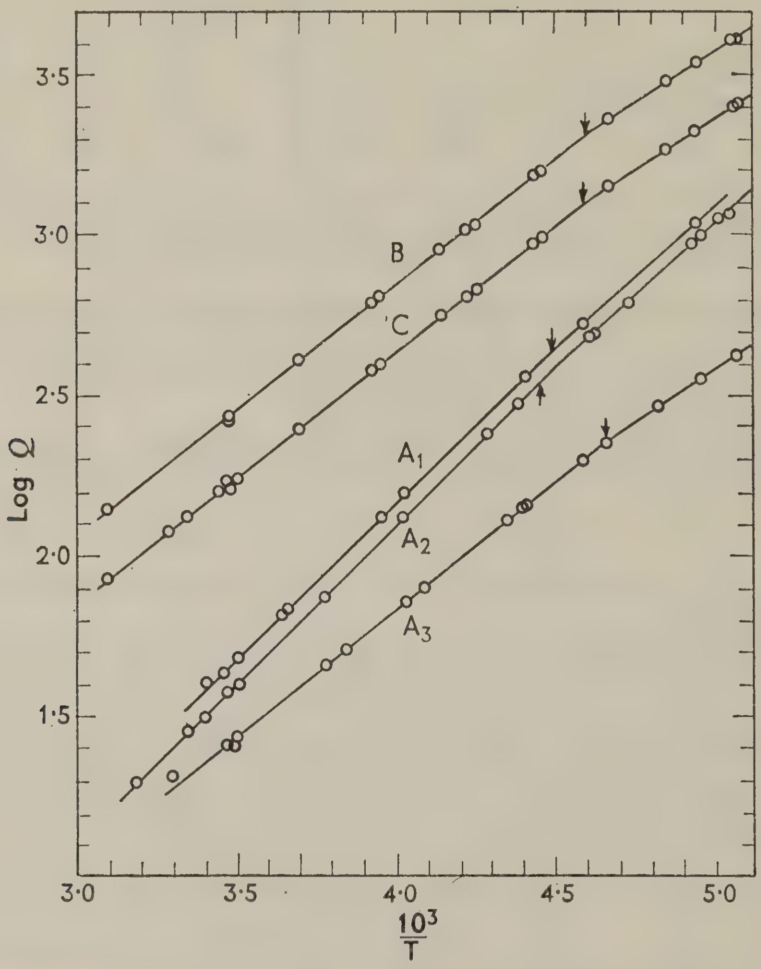

FIG. 4.—Logarithm of the specific resistance plotted against $10^3/T$ for $CuP_2$

$$4CuPX_2 \rightarrow Cu_2X + 2CuPX + P_2X_5{}^{586}$$

$CuSi_2P_3$ and $CuGe_2P_3$, which belong to a group of semiconductors of general formula $A^IB_2^{IV}C_3^V$, have disordered zinc blende structures with $a = 5{\cdot}25$ and $a = 5{\cdot}375$ A. respectively.[56] These and a series of analogues ($A^I$ = Cu, Ag; $B^{IV}$ = Si, Ge, Sn, Pb; $C^V$ = P, As, Sb, Bi) have been studied by *X*-ray and microstructure analysis.[587]

Alloys of copper with phosphorus are important industrially and several references are made in the literature to their commercial manufacture.[57–62] The copper–phosphorus system has been studied[63–4]; Fig. 5 shows the phase diagram up to 14% by weight of phosphorus. In the diagram the results of the investigators are compared with the previously determined diagram. The main investigations on copper–phosphorus alloys have dealt with thermal conductivity,[64] mechanical properties,[65–7] influence of phosphorus content on the crystallization of copper,[68] reaction diffusion[69] and the electrical properties.[65, 70] In their lubricating properties phosphorus–

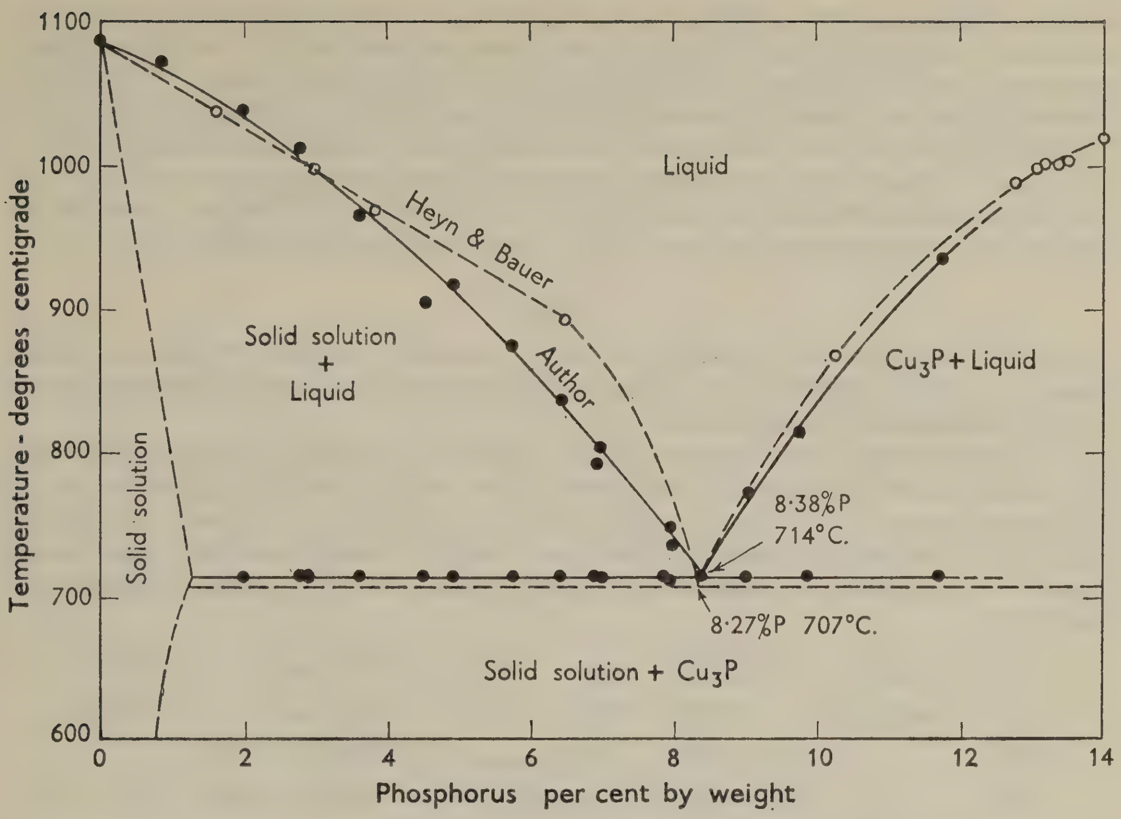

FIG. 5.—The equilibrium diagram of the copper–phosphorus system (0–14% P)

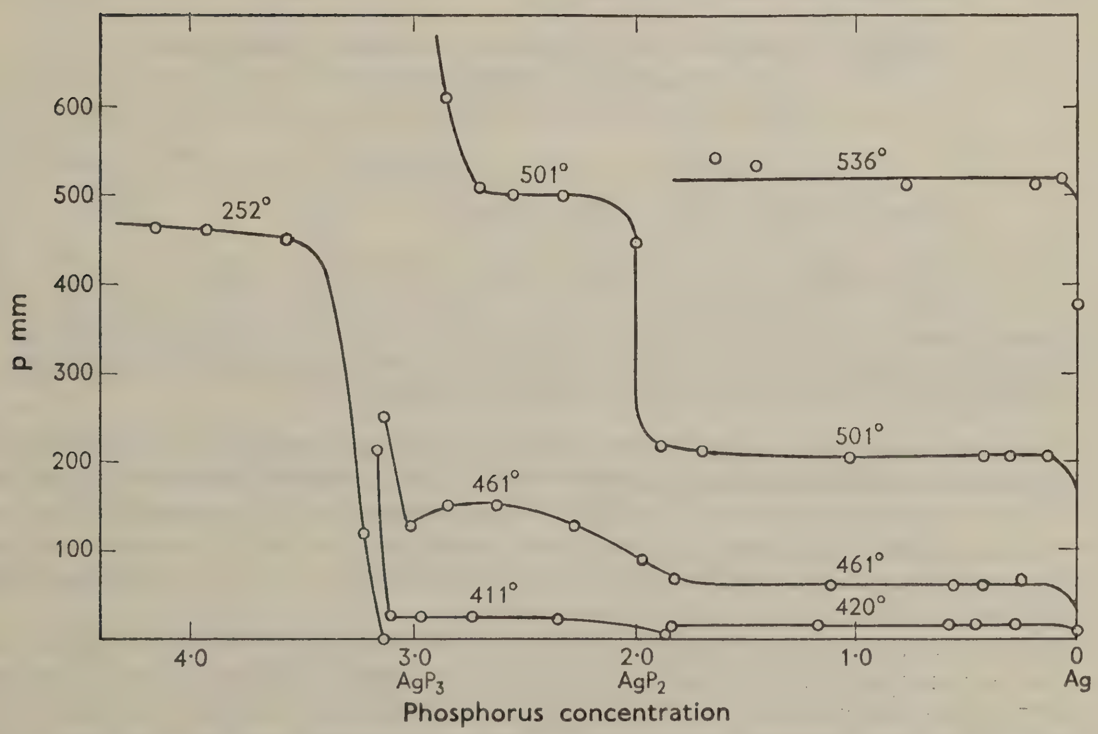

FIG. 6.—Vapour pressure–concentration diagram for the silver–phosphorus system

copper alloys have been shown to be as efficient as some sulphides but inferior to graphite.[71] Alloys or phosphides have found uses as deoxidants in metal smelting,[72] as a component of catalysts for the oxidation of phosphorus in steam,[73–4] as friction elements in brake linings or clutches[75] and as a hard solder or brazing material.[76–81] The effect of copper phosphides on the colour of copper red glass has been discussed.[82]

Ternary systems which have been investigated are copper–phosphorus–tin,[83–8, 63] copper–phosphorus–zinc,[63] copper–phosphorus–silver,[48, 89, 90] copper–phosphorus–chromium,[91] copper–phosphorus–nickel[91–3] and copper–phosphorus–iron.[94]

## Silver

Disilver phosphide is reported to have transistor properties[51] and a specific resistance at 0°C. of 0·30 to 0·33 ohms-cm.[51] This appears to be the sole reference to a silver phosphide of this formula.

Two phosphides, silver diphosphide and silver triphosphide, have been prepared by passing phosphorus vapour over heated silver and by heating together silver and red phosphorus.[48, 46, 54] V.p. measurements shown in Fig. 6[46] reveal that the two phosphides are miscible with one another. Heats of dissociation have been calculated[46, 54] according to equations (8) and (9) and the v.p. obeys equations (10) and (11)[54]:

$$(8)\quad 4AgP_3(s) \rightarrow 4AgP_2(s) + P_4(g) \qquad \Delta H = +35{\cdot}5 \text{ kcal.} \qquad \bar{t} = 456°\text{C.}$$

$$(9)\quad 2AgP_2(s) \rightarrow 2Ag(s) + P_4(g) \qquad \Delta H = +32{\cdot}9 \text{ kcal.} \qquad \bar{t} = 478°\text{C.}$$

$$(10)\quad \text{For } AgP_3 \qquad \log p_{(mm.)} = -7766/T + 12{\cdot}74$$

$$(11)\quad \text{For } AgP_2 \qquad \log p_{(mm.)} = -7186/T + 11{\cdot}60$$

The free energies of formation of solid $AgP_2$ and $AgP_3$ from the gaseous elements at $T$°K. are given by $\Delta G = -32{,}800 + 22{\cdot}5T$ g.-cal. and $-49{,}900 + 33{\cdot}8T$ g.-cal./mole, respectively.[548] Density determinations give for silver triphosphide $d = 3{\cdot}881$ g./c.c.[46] and for silver diphosphide $d = 4{\cdot}653$ g./c.c.[46] The two compounds are black and stable in the atmosphere.[54] Silver diphosphide is isostructural with copper diphosphide, the two compounds showing complete mutual solid solubility. The crystal lattice is monoclinic with $a = 6{\cdot}218$, $b = 5{\cdot}056$, $c = 7{\cdot}804$ A., $\beta = 113{\cdot}48°$.[585] Magnetic susceptibilities, measured from −183°C. to 388°C., are shown in Table IV.[42]

*Table IV.—Magnetic Susceptibilities for Silver Triphosphide and Silver Diphosphide*

| | $-\chi_g \cdot 10^6$ | | | | | Mean | $-\chi_{mol} \cdot 10^6$ | $-\chi_p \cdot 10^6$ |
|---|---|---|---|---|---|---|---|---|
| $T$°C. | −183 | −78 | 20 | 168 | 388 | | | |
| $AgP_3$ | 0·31 | 0·35 | 0·37 | 0·31 | 0·31 | 0·33 | 66 | 15 |
| $AgP_2$ | 0·28 | 0·35 | 0·35 | 0·32 | 0·32 | 0·32 | 54 | 16 |

In the above Table $\chi_g$ is the susceptibility per gram of compound, $\chi_{mol}$ is the susceptibility per molecule and $\chi_p$ is the susceptibility per atom of phosphorus.

A recent investigation of the silver–phosphorus phase system at low phosphorus concentrations shows that there is some solubility of phosphorus in silver as given in Fig. 7 and that this solution boils at 885°C.[95] In the figure $b_4f_2$ is the saturation curve of molten silver; this curve is extrapolated along $b_2f_2$ to cut the vertical axis at 885°C. which is the b.p. of silver saturated with phosphorus (1·7%). It is higher than the value obtained by Raub and co-workers.[48]

Ternary compounds AgPS and AgPSe have been prepared by direct combination of the elements, which were heated for 2–3 days at 800°C. and finally for 3–4 hr. at 1200°C. They are obtained as black vitreous masses which cannot be crystallized. They are inert to acids and warm alkali.[55] Ternary compounds of the type $AgM_2^{IV}P_3$ ($M^{IV}$ = Si, Ge, Sn, Pb) have been prepared from the elements and studied by $X$-ray and microstructure analysis.[587] The crystal lattice of $AgGe_2P_3$ is not cubic like that of the copper analogue, but distorted, with $a = 10{\cdot}3$, $b = 14{\cdot}6$, $c = 8{\cdot}9$ A.[589]

The system silver–phosphorus–copper has been investigated to determine the influence of phosphorus on silver–copper alloys.[90, 89]

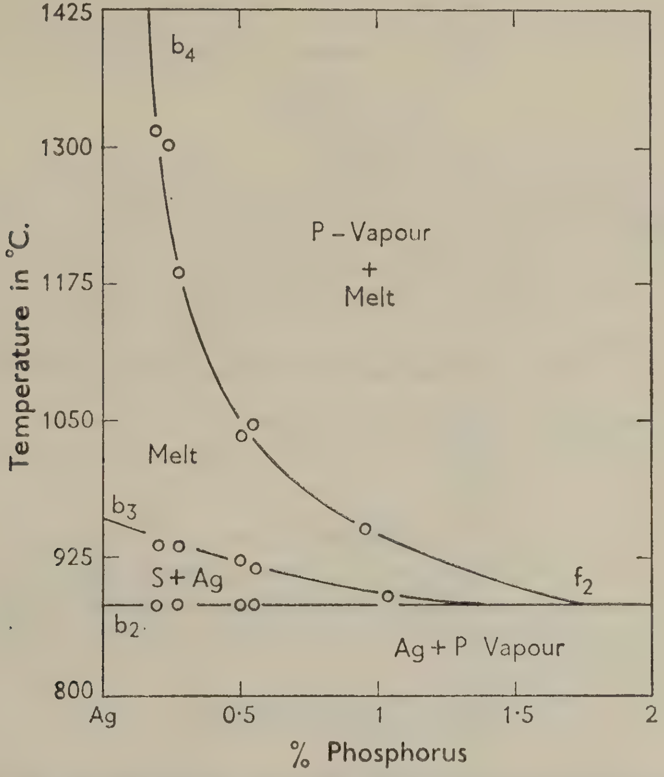

FIG. 7.—The second boiling point in the silver–phosphorus system

## Gold

By treating an auric compound in aqueous solution with phosphine it is claimed that gold monophosphide can be formed.[96] This compound is easily converted into gold under oxidizing conditions (equations (12) and (13))[96]:

$$(12) \qquad 4AuP + 5O_2 + 6H_2O \rightarrow 4Au + 4H_3PO_4$$

$$(13) \qquad 3AuP + 5AuCl_3 + 12H_2O \rightarrow 8Au + 3H_3PO_4 + 15HCl$$

Digold triphosphide is formed when gold is heated for prolonged periods at 500°C. in contact with phosphorus. It is a black compound having $d$ 8·123 g./c.c. and molecular volume 30·0 c.c.[46] The magnetic susceptibilities have been measured at temperatures ranging from −183° to 388°C.; mean values for these measurements are: $-\chi_g \times 10^6 = 0{\cdot}22$, $-\chi_{mol} \times 10^6 = 107{\cdot}0$, $-\chi_P \times 10^6 = 16$,[42] $\chi_P$ being the susceptibility per phosphorus atom. From v.p. measurements on the gold–phosphorus system, which are shown in Fig. 8,[46] the variation of v.p. of digold triphosphide with temperature was shown to obey equation (14):

$$(14) \qquad \log p_{(mm.)} = -9124/T + 12{\cdot}21$$

and the heat of disproportionation according to equation (15):

$$(15) \qquad \tfrac{4}{3}Au_2P_3(s) \rightarrow \tfrac{8}{3}Au(s) + P_4(g) \qquad \bar{t} = 630°C.$$

is $\Delta H = +41{\cdot}7 \pm 0{\cdot}2$ kcal./mole. The free energy of formation of solid $Au_2P_3$ from the gaseous elements at $T$°K. is given by $\Delta G = -57{,}500 + 33{\cdot}8T$ g.-cal./mole.[548] Results

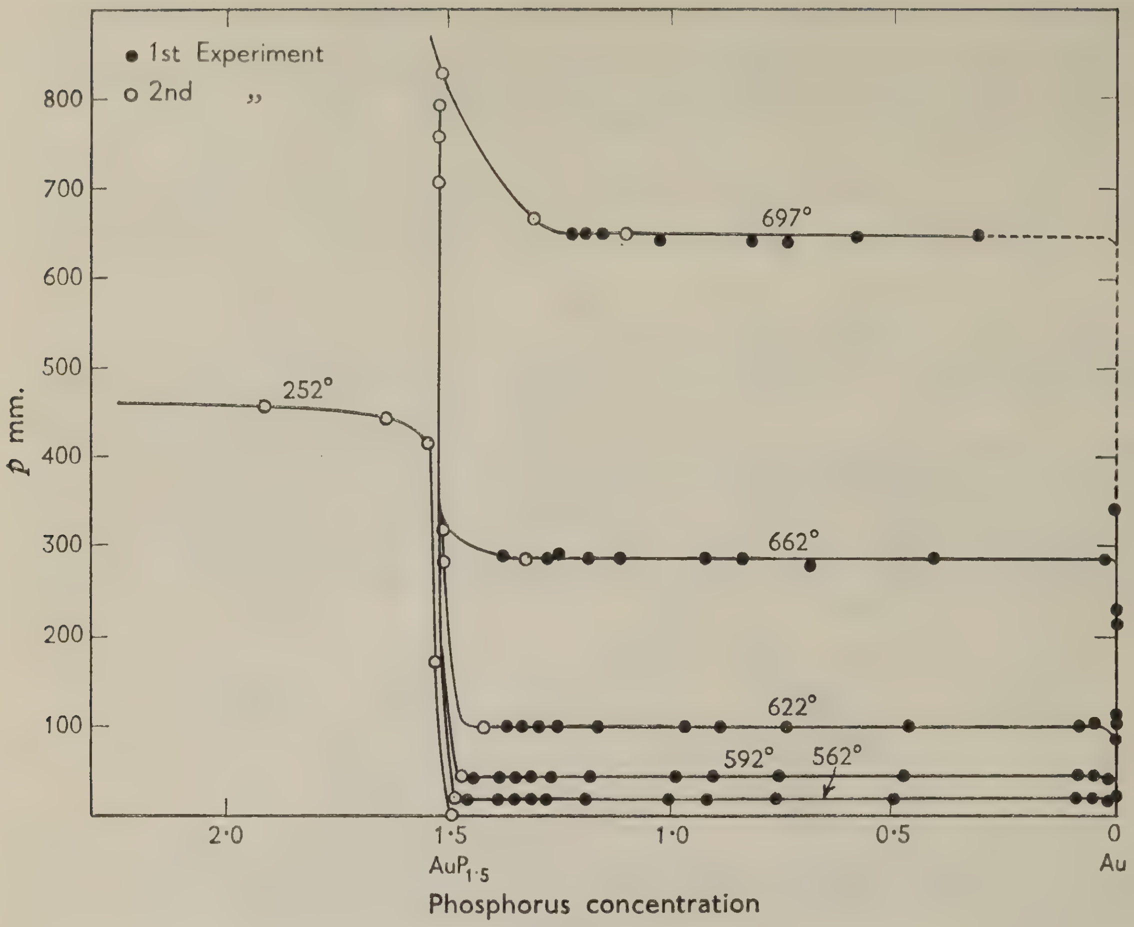

FIG. 8.—Vapour pressure–concentration diagram for the gold–phosphorus system

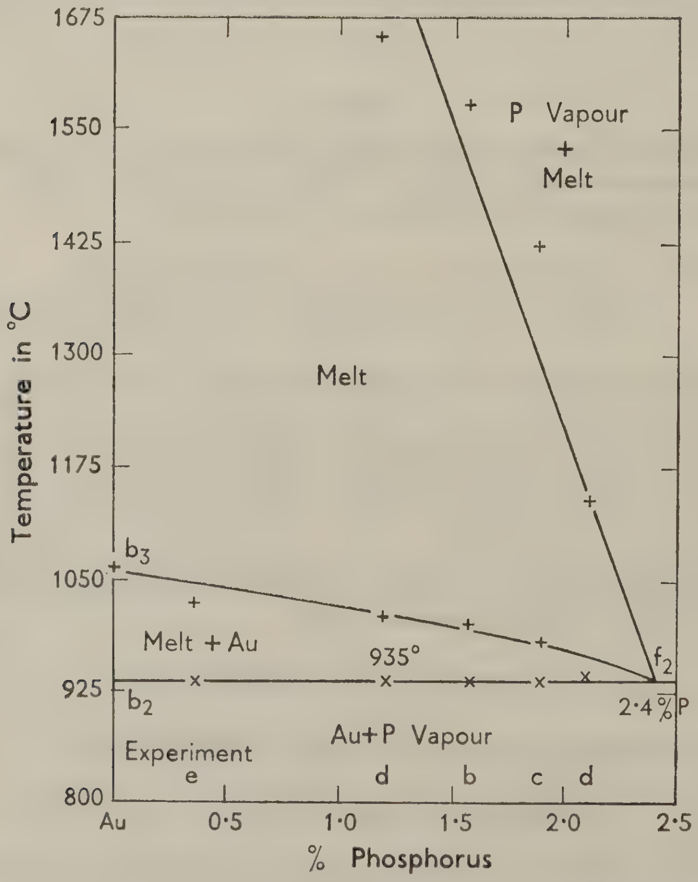

FIG. 9.—The second boiling point in the gold–phosphorus system

of specific resistance measurements are shown in Fig. 3, the value at 0°C. being $1{\cdot}24 \times 10^{-3}$ ohms-cm.[51]

Phase diagram studies on the gold–phosphorus system have been made at low phosphorus concentrations.[95] Fig. 9 shows that phosphorus is slightly soluble in liquid gold; the solubility is 2·4% at 935°C.[95]

The ternary diagram of gold, phosphorus and tin was investigated in connection with segregation phenomena.[97]

## GROUP 2A

### Beryllium

Little work has been done on the beryllium–phosphorus system but triberyllium diphosphide, which has been reported as having a cubic crystal structure with $a = 10{\cdot}17$ A., $d = 2{\cdot}25$ g./c.c. and molecular volume 39·6 c.c.[98] is thought to form an ionic lattice.[99] The anions form a close-packed lattice and the cations occupy the tetrahedral or octahedral holes.

A heat of formation of 48 kcal./mole has been estimated for beryllium monophosphide.[16]

In the system beryllium–phosphorus–iron a triangle represented by $Fe$–$Fe_2P$–$Be_2Fe$ has been investigated but no phosphides of beryllium were reported.[100]

### Magnesium

Trimagnesium diphosphide is probably the only phosphide of magnesium that exists. It has been prepared by heating the elements together in a sealed tube at 336° to 592°C.[101] and by causing magnesium to react with heavy metal phosphides[102] or even non-metallic phosphides.[582] From a high pressure study it was concluded that pressure alone would not form a phosphide from magnesium and red phosphorus[103]; in addition a shearing force was required but this may only be a device for raising the temperature. Reaction of the elements, i.e. passing phosphorus vapour in a stream of hydrogen over heated powdered magnesium was used as a method of preparing material for an *X*-ray study which showed the material to be cubic with $a = 12{\cdot}01$ A.[104] In another investigation the structure was said to be of the nickel arsenide type with $a = 5{\cdot}92$ A.[105] From these structural investigations densities 2·162 g./c.c.[105] and 2·058 g./c.c.[98] and molecular volume 65·6 c.c.[98] were determined. *K*-Emission line shift was investigated and found to be 0·15 e.v. From these investigations it was concluded that trimagnesium diphosphide possesses a strong ionic component.[106] The compound is easily hydrolyzed by water; the change of reaction velocity with time was found to be different for different specimens and this has been thought to indicate the presence of another phosphide, dimagnesium diphosphide, in the material.[101] Rough values of $-989 \pm 10$ g.-cal./g. and $-912 \pm 16$ g.-cal./g., both measured at 20°C., have been quoted for the heat of reaction with water.[107] Material obtained from magnesium turnings and phosphorus vapour gave a value $\Delta H_{20} = -989 \pm 10$ g.-cal./g., whilst a value of $\Delta H_{20} = -912 \pm 16$ g.-cal./g. was obtained for material prepared from magnesium powder and red phosphorus. The heat of formation is given as $\Delta H_f^\circ = -119 \pm 3$ kcal./mole,[108] and the free energy of formation of solid $Mg_3P_2$ from the gaseous elements is given by:

$$\Delta G = -150{,}800 + 22{\cdot}2T \text{ g.-cal./mole}$$

over the temperature range $T = 298$–$923$°K.[548] Trimagnesium diphosphide has been used as a grain disinfectant,[109–10] as a pesticide[111–3] and for removing small amounts of oxygen and other impurities from molten copper.[114]

A heat of formation of 50 kcal./mole has been estimated for magnesium monophosphide from data on oxides.[16]

A ternary composition exists; magnesium aluminium phosphide (containing the metals in the ratio by weight of 1 part of aluminium to 3 parts of magnesium) has a heat of reaction with water of approximately $-876 \pm 9$ g.-cal./g. at 20°C. It is used in sea flares.[107] $MgGeP_2$ has been shown to have the zinc blende type structure with $a = 5{\cdot}652$ A.[56]

### Calcium

Very little on the preparation of calcium phosphides has been reported in recent years. Three preparations of tricalcium diphosphide were incidental to the main studies. In the first case a study was made of the reactions of tricalcium phosphate with carbon.[115] One of the main processes which was shown to take place proceeds according to equation 16:

$$(16) \qquad Ca_3P_2O_8 + 8C \rightarrow Ca_3P_2 + 8CO$$

In the second instance a study was being made of the calcium–iron–phosphorus system and it was shown that calcium absorbs phosphorus from iron–phosphorus alloys containing more than 15% of phosphorus to form tricalcium diphosphide.[116] Finally, it was shown that calcium reacts with triphosphorus pentanitride at 200°C. to give as one of the products tricalcium diphosphide.[582] Patents dealing with its manufacture from tricalcium phosphate, carbon and water have been granted.[117] Preliminary studies indicate that the crystal structure is tetragonal with $a = b = 5{\cdot}44$ A. and $c = 6{\cdot}59$ A.[118] The compound is black–violet and has a heat of formation of $-120 \pm 2{\cdot}5$ kcal./mole[115]; a value of $-125$ kcal./mole was calculated from measurements of the heat of reaction with hydrochloric acid.[119] The free energy of formation of solid $Ca_3P_2$ from the gaseous elements is given by $\Delta G = -142{,}800 + 22{\cdot}5T$ g.-cal./mole over the temperature range $T = 298$–$1123$°K.[548] Observations on K-emission line shifts led the investigators to conclude that the compound has a strong ionic character.[106] The reaction with water is a diffusion controlled reaction which proceeds according to equation (17)[120]:

$$(17) \qquad Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

It reacts with excess of phosphorus to give calcium monophosphide[118] and is decomposed at 250° to 300°C. by a mixture of carbon dioxide and sulphuryl chloride to give calcium chloride.[121] Several patents concerned with uses for tricalcium diphosphide have been granted, the main ones being for use in markers for torpedoes,[122] as a grain disinfectant,[123] for generation of phosphine, as an activator or collector modifier in froth flotation[124] and as a pesticide.[111–3, 125]

The next higher phosphide, calcium monophosphide, has been prepared by treating calcium dissolved in liquid ammonia with phosphine and decomposing the product thermally.[118, 549] $Ca(PH_2)_2,5NH_3$ is first formed and this is decomposed below 100°C. to give CaPH which yields calcium monophosphide at temperatures between 100° and 600°C. Previous work on this system has shown that $(PH_2)_2Ca,6NH_3$ could be formed which decomposed *in vacuo* at 0°C. to give $(PH_2)_2Ca,2NH_3$. Either of these compounds, if heated *in vacuo*, yields CaPH which in turn loses hydrogen at higher temperatures.[579] The Thénard process for the manufacture of calcium monophosphide has been improved by decomposing beforehand the calcium carbonate present in the lime used, by working in a current of nitrogen, and by allowing the phosphide formed from the calcium oxide and phosphorus to cool in a nitrogen atmosphere.[126] Other compounds such as calcium chloride, calcium carbide and calcium hydride, as well as metallic calcium, have also been shown to produce either a mixture of calcium monophosphide and tricalcium diphosphide or calcium monophosphide on reaction with red phosphorus.[118, 549] Preliminary results suggest that this brick-red compound has a tetragonal crystal structure with $a = b = 5{\cdot}93$ A. $c = 7{\cdot}94$ A.[118] Heating it above 600°C. converts it into tricalcium diphosphide,[118] whilst tricalcium phosphate is produced by reaction with carbon dioxide or a mixture of phosphorus vapour and carbon dioxide. Unlike tricalcium diphosphide, calcium monophosphide does not produce phosphine on treatment with water but reacts as shown in equation (18)[118]:

$$(18) \qquad 2CaP + 4H_2O \rightarrow 2Ca(OH)_2 + P_2H_4$$

Calcium diphosphide has been shown to form phosphates when heated with alkaline earth oxides in the presence of oxygen.[127]

### Strontium

The enthalpy of formation of tristrontium diphosphide was calculated as being $-160 \pm 2$ kcal./mole from measurements of the heat of reaction of the phosphide with dilute hydrochloric acid.[128]

### Barium

Barium, heated at 400° to 450°C. in phosphorus vapour, gives a dark grey product which is probably barium triphosphide.[129] Excess of phosphorus can be removed by heating *in vacuo*. At a temperature between 740° and 840°C. phosphorus is lost until the composition approaches that of barium diphosphide. Barium diphosphide is stable under these conditions and can be confirmed tensimetrically,[129] but at still higher temperatures it decomposes further to tribarium diphosphide (Mellor, VIII, 842).

## GROUP 2B

### Zinc

Trizinc diphosphide has been prepared by reducing trizinc phosphate with hydrogen at 600°C. in a closed system,[43] or by passing phosphorus vapour over zinc heated to 400°C.[130] Experiments indicate that it is also formed merely by rubbing together red phosphorus and zinc provided sufficient pressure is applied.[103] Pure trizinc diphosphide has been prepared from pure zinc and red phosphorus in a heated evacuated quartz ampoule, and further purified by sublimation, for measurements of its electrical resistivity and thermoelectric power.[590] Processes for its manufacture have been patented. In one method trizinc phosphate is reduced at elevated temperature with carbon[131]; in a second, phosphorus and zinc react in an externally heated ball-mill,[132] whilst in a third yellow phosphorus reacts with molten zinc.[133] *X*-Ray measurements show the crystal structure of trizinc diphosphide to be tetragonal with $a = 8{\cdot}097 \pm 0{\cdot}020$ A., $c = 11{\cdot}45 \pm 0{\cdot}030$ A.[130] The $^{31}P$ nuclear magnetic resonance spectrum is in accordance with this structure,[591] showing two peaks of equal intensity, with chemical shifts of +217 and +250 p.p.m. relative to 85% $H_3PO_4$. The density is 4·54 g./c.c. and it has molecular volume 56·9 c.c.[130] It is a dark grey metallic powder, but evaporated films appear bright in reflected light and dark red in transmitted light.[134] Trizinc diphosphide is decomposed by fusion with sodium hydroxide in air, according to the initial reaction

$$2M_xP_2 + 6NaOH + O_2 \rightarrow 2xM + 2PH_3 + 2Na_3PO_4 \tag{18a}$$

The zinc then undergoes further reactions with the formation of zincates.[593] In agreement with earlier work,[135] it is found that this phosphide sublimes at 1000°C. without decomposition.[136] A value of $-98 \pm 3$ kcal./mole was obtained for the heat of formation from the elements,[137] but this value differs from a previously determined value of $-55{\cdot}03 \pm 1{\cdot}5$ kcal./mole[138] and therefore the heat of hydrolysis was measured. From the hydrolysis measurements a figure of $-53{\cdot}37 \pm 0{\cdot}35$ kcal./mole was obtained[139] for the heat of formation of trizinc diphosphide. It has been shown that the phosphorescence of this compound is extinguished by infra-red radiation.[140] In studies on the electrical and optical properties it has been demonstrated that trizinc diphosphide can act as an *n*-type or *p*-type semiconductor material. The *n*-type material shows poor rectification characteristics.[134, 141–2, 51] Reports on the uses have been mainly connected with its toxicity,[143–58] although patents refer to its use as a catalyst in the preparation of aliphatic nitriles from aliphatic alcohols[159] and acetone from *iso*propyl alcohol.[160] Its heat transfer properties have also been investigated.[161] It has been reported that zinc phosphide is not completely destroyed in food cooking processes.[162]

Zinc diphosphide is prepared by heating zinc to approximately 700°C. and passing over it a stream of nitrogen containing phosphorus vapour.[130] The compound is yellowish-orange in colour and sublimes at 700°C. in phosphorus vapour, but decomposes to give trizinc diphosphide if heated to 700°C. *in vacuo*.[130] The crystal structure has been shown to possess tetragonal symmetry with $a = 5{\cdot}07$, $c = 18{\cdot}65$ A.[130] Densities by various methods agree quite well: 3·51 g./c.c. (*X*-ray), 3·56 g./c.c. (pyknometer), 3·53 g./c.c. (flotation).[130] It is practically insoluble in non-oxidizing acids,[130] but is decomposed by fusion with sodium hydroxide in air according to equation (18a) with further reaction of the zinc to zincates.[593]

If zinc is treated with phosphorus in a closed system, on the other hand, two forms of zinc diphosphide are formed, their ratio depending on the pressure of phosphorus vapour in the system. At 3 atm. and 700° to 850°C. the product contains 50% of the form described above (red tetragonal crystals, $a = 5{\cdot}08 \pm 0{\cdot}01$, $c = 18{\cdot}59 \pm 0{\cdot}05$ A., space group $P4_12_12$ or $P4_32_12$). The remainder is a new form of $ZnP_2$, which at 10 atm. is the sole product. It forms black monoclinic crystals, $a = 8{\cdot}85 \pm 0{\cdot}02$, $b = 7{\cdot}29 \pm 0{\cdot}02$, $c = 7{\cdot}56 \pm 0{\cdot}02$ A., $\beta = 102{\cdot}3 \pm 0{\cdot}2°$, density 3·47 g./c.c. *X*-Ray study of the product discloses no $Zn_3P_2$, and its structure resembles that of $ZnAs_2$. Optical absorption (red and black) photoluminescence (red) and photoconductivity (black) data are recorded.[550] A detailed crystal structure has been determined for the tetragonal modification. All the atoms are tetrahedrally co-ordinated, with each zinc atom bonded to four phosphorus atoms, and each phosphorus to two zinc and two phosphorus atoms.[592]

Ternary compounds which have been reported, zinc silicon diphosphide, zinc tin diphosphide and zinc germanium diphosphide, were prepared from phosphides of Group III elements.[163–4, 56, 594–5] They have the chalcopyrite structure with $a = 5{\cdot}398$ A. and $c/a = 1{\cdot}934$ for zinc silicon diphosphide and $a = 5{\cdot}46$ A., $c/a = 1{\cdot}97$ for zinc germanium diphosphide.[56, 163, 165, 594] Physical,[594] electric and photoelectric[166, 595–6] and optical[596] properties of these compounds have been discussed.

The phase diagram zinc–phosphorus–iron[167] and a small portion of the liquidus of the system zinc–phosphorus–copper[63] have been investigated.

### Cadmium

Tricadmium diphosphide is formed when cadmium diphosphide is heated *in vacuo* at 700°C. It is metallic grey,[130, 597] brittle and fairly hard. It melts peritectically at 739 ± 2° giving a mixture of cadmium and cadmium diphosphide,[597] and its heat of formation is −27·4 kcal./mole.[168] In a structural investigation the crystal structure was shown to be tetragonal with $a = 8{\cdot}746 \pm 0{\cdot}02$, $c = 12{\cdot}28 \pm 0{\cdot}03$ A.[130] Density $5{\cdot}60 \pm 0{\cdot}06$ g./c.c. and molecular volume 71·2 c.c. were calculated from the *X*-ray data.[130] Specific resistance measurements are shown in Fig. 3 (page 294).[51] Other values have been given for the specific resistance, as well as for the Hall effect,[597] thermoelectric power and semiconducting properties.[598] It is stable in water and non-oxidizing acids.[130]

Cadmium diphosphide has been prepared by heating the elements together in a sealed tube at approximately 600°C.[130, 599] and by subliming tricadmium diphosphide in a phosphorus-rich atmosphere.[130] The dark crystals distil at 640°.[599] The solid crystallizes with tetragonal symmetry having $a = 5{\cdot}28$ A., $c = 19{\cdot}70$ A. and $d$ 4·19 g./c.c.[130] The compound is similar to zinc diphosphide in being unaffected by water and only slightly affected by acids.[130] Transmittance measurements at room and liquid nitrogen temperatures show a strong infra-red absorption which, together with the very high optical activity of single $CdP_2$ crystals, points to a very large contribution by ionic bonding in the lattice.[599]

In experiments designed to give $CdPbP_{14}$ a black product was sometimes obtained which did not show the properties expected of a Group II-metal lead polyphosphide.[169] Further investigation showed it to be cadmium tetraphosphide. It was also prepared by heating purified white phosphorus with a cadmium–lead alloy at 565°C. for 2½–5 days,[170] or from the elements in a quartz double zone furnace held at 700° and

450°, respectively.[600] It has a monoclinic crystal structure, space group $P2_1/c$, with $a = 5{\cdot}26$, $b = 5{\cdot}18$, $c = 7{\cdot}64$ kx. units and $\beta = 80°\ 32'$. The electrical conductivity is 2 ohms$^{-1}$ cm.$^{-1}$ and the thermoelectric power 600 μv/°C.[600] This compound appears to be very inert to chemical attack, dissolving only slowly in hot aqua regia,[170] but when heated *in vacuo* it decomposes into its elements.[170]

The compound $CdPbP_{14}$ has been prepared by reaction of red phosphorus with an alloy of lead and cadmium at temperatures between 525° and 610°C. for 8–10 days.[169] It shows only slight chemical reactivity, dissolving slowly in concentrated sulphuric and nitric acids.[169] Other ternary phosphides are cadmium germanium diphosphide, cadmium silicon diphosphide, and cadmium tin diphosphide.[164] The first of these has the chalcopyrite structure and an energy gap of 1·8 e.v.[164] It has been discussed from the point of view of its use in semiconductor devices.[166] Cadmium tin diphosphide has an energy gap of 1·5 e.v.[164] Cadmium silicon diphosphide also crystallizes in the chalcopyrite structure ($a = 5{\cdot}678$, $c = 10{\cdot}431$ A.). Values of its melting point, microhardness, and energy gap have been recorded.[594]

Ternary cadmium phosphide halides of the general formula $Cd_4P_2X_3$ (X = Cl, Br, I) have been described. They all form deep orange cubic crystals and melt incongruently below 600°C. The bromide has a density of 5·29 g./c.c. and is unaffected by water or benzene at room temperature.[551]

### Mercury

A phosphide compound containing iodine has been reported.[171] White phosphorus is said to react with mercuric iodide suspended in carbon disulphide to give, upon evaporation of the solvent after fifteen days, a yellow dimercury di-iodine phosphide. A mixed lead mercury phosphide is mentioned under lead on page 313.

## GROUP 3

A great deal of attention has been given to Group III phosphides in recent years and in particular to indium phosphide and gallium phosphide. Most of the work has been done in connection with their semiconducting properties and, since the material belongs to the realm of physics rather than chemistry, information on such matters should be sought in more appropriate places.[172–4]

### Aluminium

In contradiction to previous reports (Mellor, VIII, 846), aluminium appears to form only the monophosphide, AlP. This has been prepared by reaction of phosphorus vapour with aluminium powder at 500°C.,[175] red phosphorus with aluminium at temperatures above 400°C.,[176–7] cadmium phosphide with aluminium[601] or aluminium chloride,[602] or by heating purified zinc phosphide with aluminium at 800° to 900°C. for 5 hr.[136, 552] In this last method almost quantitative yields were obtained. Patents have been granted for its manufacture from the elements,[178] from the elements plus carbon,[179] and also from zinc phosphide and aluminium.[180] The preparation of aluminium phosphide of semiconductor quality has been described.[553] Crystalline aluminium phosphide has a cubic zinc-blende type lattice with $a = 5{\cdot}42$ A.,[105] $a = 5{\cdot}451$ A.,[175–6, 136, 181] $5{\cdot}467 \pm 0{\cdot}002$ A.[552] Although it is very similar to zinc sulphide the solubility of aluminium phosphide in zinc sulphide is very limited, probably not in excess of 1 mol-%.[182] The colour of aluminium phosphide, which has $d$ $2{\cdot}40 \pm 0{\cdot}01$ g./c.c.[552] and a Mohs hardness of 5·5,[175] varies from dark grey to yellow for samples of the highest purity.[176] The melting point has been given as 1350°C. and the energy gap 3·1 e.v.,[608] though other workers[687] have claimed the melting point to be above 2000°C. A heat of formation of 66 kcal./mole has been estimated for the gaseous phosphide, using oxide data as a guide,[16] whilst from *K*-emission line shift observations it has been concluded that this compound has a strong ionic component.[106] An experimental determination gave a value of $-29 \pm 2$ kcal./mole for the heat of formation of AlP at 25°C.,[552] which is in reasonable agreement with the value $-39{\cdot}5 \pm 0{\cdot}5$ kcal./mole obtained by dissolution of the phosphide in hydrochloric acid at 22°C.[603] Other values of the heat capacity and enthalpy of aluminium phosphide have been recorded.[604] Phosphors with yellow emission can be prepared by diffusing aluminium phosphide into zinc sulphide at 900°C.[182] Several chemical properties have been investigated by different authors with conflicting results. The phosphide is said to be rapidly hydrolyzed by water, acids and alkalis.[183, 176] A typical reaction is given in equation (19):

$$2AlP + 3H_2SO_4 \rightarrow 2PH_3 + Al_2(SO_4)_3 \tag{19}$$

Dry hydrogen chloride decomposes it but it can be heated in hydrogen to 1000°C. without showing loss of weight.[176] This work is supported to some extent by others[136] who report that it has a low v.p. at 1000°C., has a faint smell of phosphine, reacts violently with concentrated or dilute hydrochloric acid and explodes with 1:1 aqua regia. It is reported though that after weeks in water it is still possible to detect the *X*-ray diffraction pattern of aluminium phosphide in the samples.[136] It may be that the formation of aluminium hydroxide gel tends to protect any unchanged phosphide or that the presence of aluminium or phosphorus in samples catalyzes their reaction. Investigators who question this work[177] report that aluminium phosphide is only slightly affected by boiling water, hot concentrated hydrochloric acid, nitric acid, and aqua regia. They also report that heating in air converts the phosphide to oxide, that hot 30% potassium hydroxide liberates phosphine and that an alkali fusion gives aluminium phosphate. Agents such as bromide, iodine in benzene, lead chromate or sodium carbonate, have little effect. Oxidizing agents are reduced. Other work has shown that if adequate precautions are not taken to provide an inert atmosphere the product may contain nitrogen or even carbon from carbon-containing atmospheres such as coal gas.[184] More recently it has been shown that good yields of pure aluminium nitride can be obtained by reaction of aluminium phosphide with nitrogen at 1375–1600°.[605] A further study of the oxidation shows that finely divided aluminium phosphide takes up oxygen interstitially at 650–700°. There is no appreciable change in lattice dimensions, but the compound changes colour from grey-green to orange-brown. Above 700° aluminium phosphide reacts with dry oxygen to give aluminium phosphate. Aluminium phosphide containing interstitial oxygen will evolve phosphorus when heated *in vacuo*, while unoxidized material is thermally stable under the same conditions.[606] There is no doubt that commercial preparations react with water since they have been used as a fumigant,[110, 185], and as a pesticide.[111–3, 186–8, 546] Aluminium phosphide has been incorporated into catalysts for the oxidation of phosphorus in steam,[74] or for the polymerization of olefins,[607] and patents have been granted for its use in high efficiency photo cells[189] and semiconductor devices.[190]

Ternary systems aluminium–phosphorus–germanium and aluminium–phosphorus–silicon have been investigated at low phosphorus concentrations.[191] Phosphorus in silicon–aluminium alloys is important since the phosphorus tends to form aluminium phosphide which then provides nuclei for crystallization of the alloys.[192–3]

### Gallium

Vacuum spark excitation of GaP has revealed the molecular species GaP, $Ga_2P$, and $GaP_2$, as their positive ions.[194]

Gallium monophosphide has sprung into prominence because of the importance attached to semiconducting materials[195] and several methods of preparation have been studied. The well-known method of heating the elements together in an evacuated sealed tube or one containing an inert atmosphere has been applied.[178, 196–7, 578] Other useful methods involve the decomposition of gallium chloride, gallium nitride, gallium oxide or gallium hydroxide in a stream of phosphine.[198–203] A stream of hydrogen containing phosphorus vapour can be used instead of phosphine[204, 175] and heating gallium with another phosphide such as zinc phosphide[136] or with phosphorus trichloride[199] has been used successfully. This last method is considered to be the most promising for the preparation of highly pure gallium phosphide.[199] Gallium phosphide can also be crystallized from a solution of gallium and phosphorus in bismuth metal, well below the melting point of GaP. The product is purified by treatment with concentrated nitric acid.[609] Finally, solid gallium phosphide has been shown to react with water vapour in a stream of hydrogen to give volatile species which redeposit gallium phosphide on cooling. The reaction can be represented as:

$$2GaP(s) + H_2O(g) \rightleftharpoons Ga_2O(g) + P_2(g) + H_2(g)$$ [610]

Many methods for the preparation of gallium phosphide have been patented,[200, 205–7, 180, 208–10, 554, 602, 611] whilst several investigators have reported on methods of growing large multicrystalline or single crystal specimens, mainly by vapour phase deposition techniques.[211–9] Vibrational mixing has been shown to decrease reaction times in the preparation of gallium phosphide,[220] whilst a study of reaction times for the reaction given in equation (20):

$$Ga_2O_3 + 2PH_3 \rightarrow 2GaP + 3H_2O \tag{20}$$

showed that at 750°C. the yield of phosphide increased linearly with time from 31·98% after 1 hr. to 58·33% after 5 hr. At 950°C. the yield of 98·66 to 100% was practically independent of time.[201] The preparation of semiconductor-grade gallium phosphide has been described.[555] Crystalline gallium phosphide has the cubic zinc-blende type of structure; reported values for the unit cell dimension vary from $a = 5{\cdot}436$ A. to $a = 5{\cdot}4506$ A.[175, 196, 221–2, 200–1, 181, 202] The density is given as 4·10 g./c.c.[609] Infra-red absorption measurements show an absorption at 14μ[233] which has been attributed to a lattice vibration. Evidence is also presented which supports the fact that the anharmonic mechanism is predominantly responsible for the infra-red absorption in the combination bands. The Raman spectrum of polycrystalline gallium phosphide has been recorded, excitation being by a 6328 A. He–Ne laser beam.[616] The refractive index of gallium phosphide for infra-red radiation varies from 3·4595 at 0·5μ to 3·0137 at 4·0μ.[617] For magnetic susceptibilities good agreement between theoretical and observed values has been reported.[224] Measurements between 60°K. and the m.p.[225–6] show that the diamagnetic susceptibility decreases with increasing temperature, the Van Vleck component (which arises because of deformation of electron clouds in the atoms) of gallium phosphide having a band width of 2·28 e.v. is $\chi_p = 27{\cdot}54 \times 10^{-6}$.[227] V.p. measurements have been made and the variation of v.p. with temperature is given by the following equations

(21)[228] $\log p_{(mm.)} = -10770/T + 9{\cdot}996$
(21a)[556, 614, 619] $\log p_{(mm.)} = -18870/T + 13{\cdot}60$ $(T = 781\text{–}1005°K.)$
(21b)[612, 614, 619] $\log p_{(mm.)} = -21570/T + 13{\cdot}021$ $(T = 1035\text{–}1380°)$

At the m.p. (1467 ± 3°C.[557]) the pressure of phosphorus above the material has been reported to be 13·45 atm.,[228] greater than 13·5 atm.[229] and 35 ± 10 atm.[557] From Schröder's equation $\log x = A/T + B$, where $x$ is the mol. % of GaP, an extrapolation to 100 mol. % gave for gallium phosphide a melting point of 1522°C. and an average latent heat of fusion for temperatures below 1270° of 30·7 ± 1·1 kcal./mole.[612] The heat of formation is variously reported as −29·1 ± 2·5,[613] −24·4 ± 1·25,[614] −42·75[610] and −49·51 ± 2·97[228] kcal./mole, the standard states of the elements taken accounting for some of the divergency of results. The standard entropy $S°$ is given as 14·4 g.-cal./degree/mole.[610] The following values of incremental heat content and entropy have been reported for $GaP_{0{\cdot}996}$[615] (see also reference 604).

| $T$(°K.) | $H_T - H_{298{\cdot}15}$ (g.-cal./mole) | $S_T - S_{298{\cdot}15}$ (g.-cal./°/mole) |
|---|---|---|
| 400 | 1,110 | 3·2 |
| 800 | 5,840 | 11·36 |
| 1200 | 10,790 | 16·37 |
| 1500 | 14,600 | 19·2 |

Hardness measurements, made by the Knoop method, show that gallium phosphide obeys the Goldschmidt Rule, $\log H = k - m \log r$ where $m$ is approximately 9, $r$ is the interatomic distance, $H$ is the scratch hardness expressed in Mohs numbers and $k$ is a constant.[230] The hardness, expressed in Mohs numbers, has been given as approximately 5·0.[175] An investigation into the bond character of phosphides showed that, like indium phosphide, gallium phosphide has a strong ionic component.[106] Other investigators showed that it differs from indium phosphide in not exhibiting a pressure-induced transition at up to 550 kilobars pressure.[231] Various etching techniques have been investigated.[232–3, 197] Gallium phosphide forms a continuous series of solid solutions with gallium arsenide[234–6] the cell dimensions of which follow a linear relationship[235] (see Vegard's Law[237]). Similarly it has been shown to form a continuous series of solid solutions with indium phosphide.[238] Gallium phosphide is a yellow compound, insoluble in water but soluble in inorganic acids and bases.[202] It reacts with solid sodium hydroxide in air, according to the equation

$$4GaP + 6NaOH + O_2 \rightarrow 4Ga + 2PH_3 + 2NaPO_3$$ [618]

Possible outlets for gallium phosphide as a semiconducting material have been discussed.[239–42, 190] Its Verdet constant,[243] which is larger than that of carbon disulphide or nickel tetracarbonyl in the visible region, makes it a possible material for use in Faraday cells.[244] Gallium phosphide diodes show avalanche breakdown in a similar manner to silicon diodes and they may show advantages over such devices as sources of very fast light pulses.[245] Patents have been granted on its use in photo cells.[189, 246] It has been considered as a heat transfer fluid in atomic energy work.[161] When an electric current is passed through $p$–$n$ junctions in Ga(AsP) semiconductors at 77°K., stimulated emission of coherent visible radiation ($\lambda = 7100$ A.) is observed.[558]

## Indium

Indium forms only a monophosphide. It was first prepared by heating together the calculated proportions of the two elements *in vacuo*.[247] The reaction was very slow and even after 400 hr. at 700°C. the yield was not 100%. Other investigators have used this method of preparation[248–9] as well as one involving the reaction of indium with zinc phosphide.[136, 180] The compound has also been produced by a continuous flow vapour phase reaction in the presence of an unreactive carrier gas, by direct reaction in the liquid phase, by the reaction of phosphine with indium chloride,[199] oxide[620] or hydroxide,[621] and by a replacement reaction starting with indium and phosphorus trichloride.[199] The last mentioned method may be worth investigating as a method for the production of very pure indium phosphide since zone melting is said to give only a small increase in purity.[250] On the other hand a patent specification claims the preparation of spectroscopically pure material from indium oxalate and phosphine at 300°C.[251] Hydrogen reduction of a mixture of indium chloride and phosphorus trichloride vapour also yields indium phosphide.[554] The preparation of semiconductor grade indium phosphide has been described.[559, 622] Reductions in reaction times in the preparation of indium phosphide by working at higher temperatures with pressure compensated vessels[252] and by employing vibrational mixing of components have been claimed.[220] A method of preparation based on a directional crystallization from a melt in a temperature gradient has been outlined.[253] Because of the great interest in this compound as a semiconductor material several patents for its manufacture have been obtained.[178, 250, 254–7, 207, 209–10, 602]

It is a dark grey material and has a metallic appearance.[247, 136] Its refractive index is given by the relations[629]:

$$n^2 = 7{\cdot}255 + 2{\cdot}316\lambda^2/(\lambda^2 - 0{\cdot}3922 \times 10^8) \quad \text{at } 298^\circ\text{K.}$$

and

$$n^2 = 7{\cdot}781 + 1{\cdot}661\lambda^2/(\lambda^2 - 0{\cdot}4397 \times 10^8) \quad \text{at } 77^\circ\text{K.}$$

Several *X*-ray measurements have been made on this cubic zinc-blende type material giving cell dimensions varying from

$$a = 5{\cdot}8688 \pm 0{\cdot}0001\ \text{A.} \quad \text{to} \quad a = 5{\cdot}8693 \pm 0{\cdot}0006\ \text{A.}^{258,\ 222,\ 181,\ 620}$$

Two different investigators have measured the intensities of *X*-ray diffraction powder lines and report agreement with calculated values, but unfortunately the two sets of

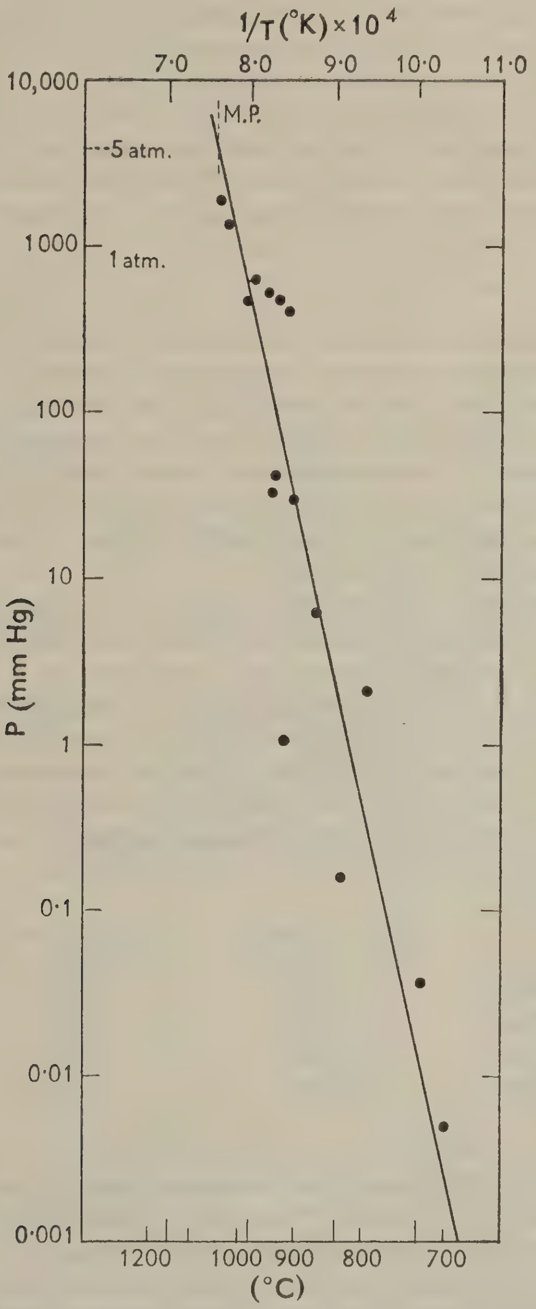

FIG. 10.—Dissociation pressure of InP from 700° to 1045°

experimental values do not agree very closely.[136, 247, 181] Deductions concerning the bonding in this compound have been made from calculations concerning the effective charge on the atoms,[259] from spectrographic measurements,[106] and from dissociation pressures and cohesion energies.[260] The cohesive energy for a purely ionic compound was calculated to be 84,000 g.-cal./mole whilst the dissociation energy of indium phosphide into liquid indium and phosphorus at a temperature below 900°C. was estimated to be 26,000 g.-cal./mole. V.p. measurements (shown in Fig. 10), together with a known heat of vaporization of indium and a known heat of dissociation of $P_4$ allowed a cohesion energy of 154,000 g.-cal./mole to be calculated. From these facts the investigators concluded that indium phosphide is mainly covalent[260] although in contrast other workers have claimed that it contains a strong ionic component.[106] The vapour pressure data presented in Fig. 10 fit equation (22)

$$\log p_{(\text{mm.})} = -23{,}000/T + 21\cdot0 \tag{22}$$

From the figure it can also be seen that the pressure of phosphorus over indium phosphide at the m.p. is 5 atm.[260] This is at variance with other values of 15·5 atm.,[229] 21 ± 5 atm.[557] and 60 atm.[261] (see also references 623, 624). M.p. data appear to be in good agreement with reported values of 1062 ± 7°C.,[261] 1062°C.,[262] 1070°C.,[260] 1050°C.,[248] 1058 ± 3°C.[557] and 1054 ± 5°C.[263] Piezo resistance measurements at 77°K. and 300°K. have been interpreted on the basis of a spherical conduction band with a minimum at the centre of the Brillouin zone,[264–5] but the investigators were unable to substantiate the existence of a second higher band.[264] Magnetic susceptibilities show good agreement with theoretical values; at 20°C.

$$-\chi_g \times 10^6 = 0\cdot313 \quad \text{and} \quad -\chi_{\text{mol}} \times 10^6 = 45\cdot6^{224-6}$$

It is thought that pressures of the order of 130 to 135 kilobars induce solid–solid type transitions to a conducting state which is apparently metallic.[231] A form of indium phosphide having a sodium chloride type lattice has been demonstrated at pressures of 22–130 kilobars.[560] The melting point of indium phosphide decreases by 2·9°C./kilobar up to 70 kilobars.[561] Measurements of conductivity at ordinary pressures and down to 1·5°K. have also been made but no evidence for superconductivity was found.[266] The thermal conductivity and Seebeck effect of indium phosphide have been measured between 300° and 800°K.[627]

Etching characteristics and formation of dislocation pits on {111} planes have been investigated[267]; etching methods have been developed to reveal the microstructure of polished specimens whose microhardness was being investigated. A value of 431 kg./mm.[2, 268] was obtained for the microhardness, which follows Goldschmidt's Rule.[230] From mass spectroscopy measurements on the composition of the gas phase above indium phosphide, it has been calculated that the free energy of formation at 1000°K. is −9200 g.-cal./mole and the entropy at this temperature is 25 e.u.[269] (see also reference 562). The following values of incremental heat content and entropy have been reported[615] (see also reference 604)

| $T$°K. | $H_T - H_{298\cdot15}$ (g.-cal./mole) | $S_T - S_{298\cdot15}$ (g.-cal./°/mole) |
|---|---|---|
| 400 | 1,150 | 3·31 |
| 800 | 5,920 | 11·57 |
| 1200 | 11,010 | 16·71 |
| 1300 | 12,400 | 17·82 |

For the standard heat of formation $\Delta H_f^\circ$ (298·15°) values of −11,[625] −21·5 ± 1·5[613] and −21·2 ± 1·0[626] kcal./mole have been recorded. Heats of fusion calculations have given a value of 15,200 g.-cal./mole[270] (see also reference 628). A series of experiments on sandblasting with various compounds (alumina, silica, steel powder, etc.) in a variety of gases (air, hydrogen, helium, etc.) showed that indium phosphide is triboluminescent.[271] Phase work has shown the indium–phosphorus system to be of the monotectic type; the various investigations are reproduced in Figs. 11,[261] 12,[262] 13[270] and in Table V data are reproduced for the system $InP/In_2Se_3$ in which mixed crystal formation starts at 33·3 mol.-% indium phosphide.[272] Alloys in this system which have compositions close to indium phosphide have a zinc-blende type lattice as have alloys $9InP$–$In_2Se_3$ and those extending from $4InP$–$In_2Se_3$ to $InP$–$In_2Se_3$. Decrease in lattice parameters with increase in $In_2Se_3$ content indicates solid solution effects in these alloys.[273] With indium arsenide[234, 274] or gallium phosphide,[238] indium phosphide forms continuous series of solid solutions, although the cell dimensions in the indium arsenide series do not obey Vegard's Rule.[274] Mainly because of the interest in indium phosphide an investigation was undertaken into the conditions under which it bonds to various metals and alloys.[275] Review articles on methods of preparation, properties and applications of intermetallic semiconductors include references to indium phosphide.[249, 240]

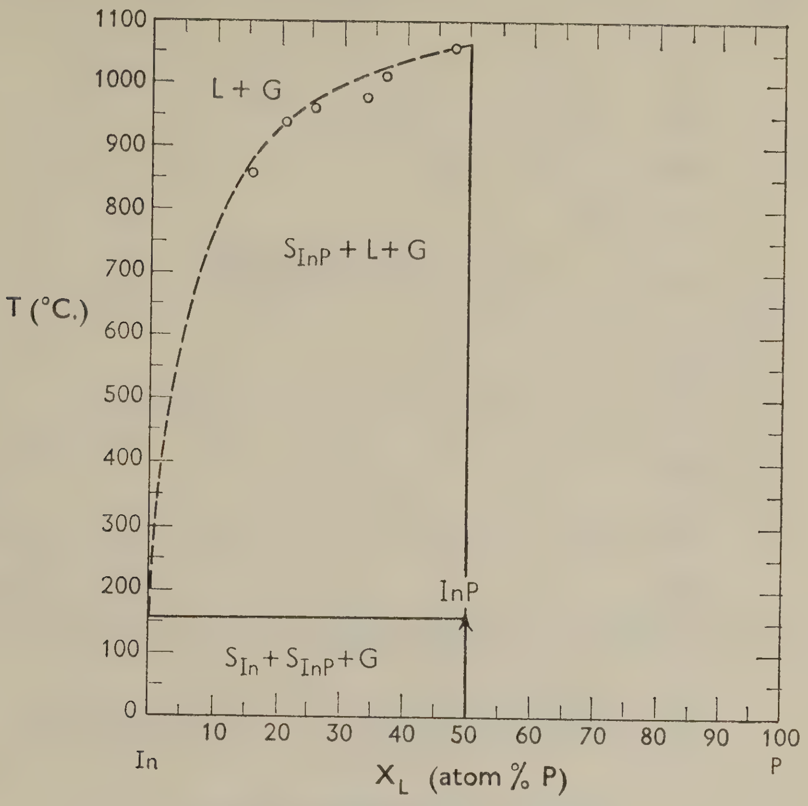

FIG. 11.—*T–x* projection of the system In–P

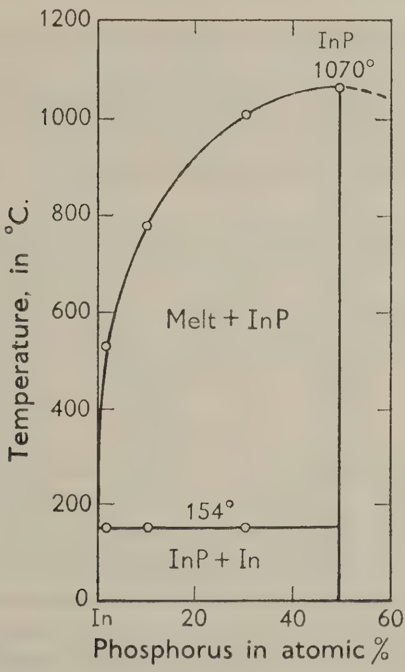

FIG. 12.—Indium–phosphorus phase diagram

The compound is stable to air oxidation and is not attacked by concentrated mineral acids,[247] acetic acid,[263] water or alkali.[276, 263] Hot solid sodium hydroxide decomposes the phosphide in air, with formation of indium, phosphine and sodium metaphosphate.[618] Dilute acids, hydrochloric, sulphuric or nitric readily form phosphine.[276, 263] Oxidation of indium phosphide crushed in a vacuum was studied by measuring the uptake of oxygen at 26°C. by the freshly prepared surfaces. The reaction does not appear to involve a distinct metastable complex before formation of the true oxide as has been observed with several Group III-Group V compounds.[277] Indium phosphide possesses useful rectification properties and shows a transistor effect[263, 278] although the evidence for the latter has been doubted.[279] Its possible use as a photovoltaic solar energy converter has been predicted[280] and a patent issued.[189] Measurements of the Faraday effect show that its Verdet constant is large enough to make it useful in Faraday cells[244] and the possible use of indium phosphide as a semiconductor operating at high temperatures has been discussed.[239, 281–3, 208, 190]

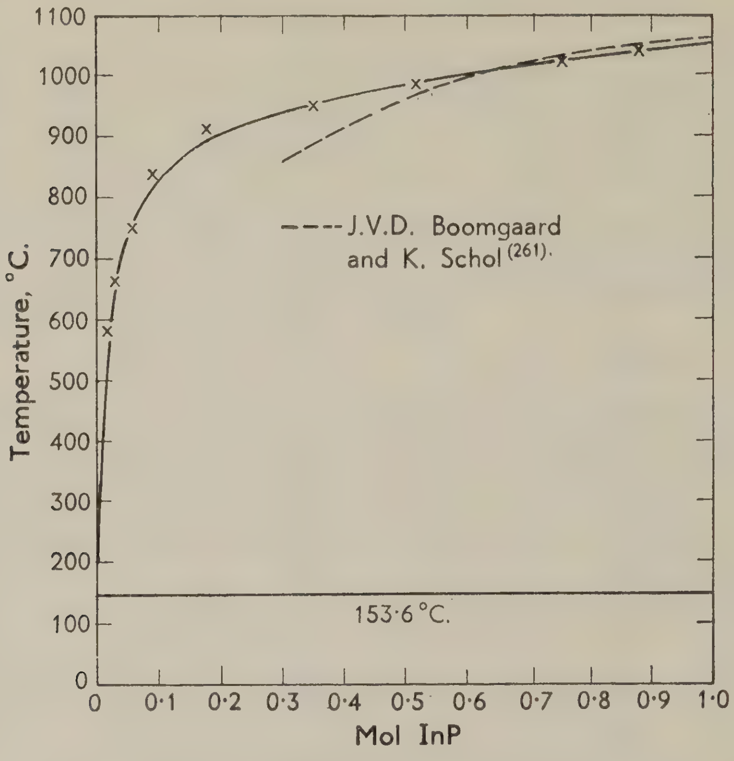

FIG. 13.—Phase diagram In–InP

*Table V.—Cell Constants and Densities in the* $InP/In_2Se_3$ *System*

| Mol % InP | *a* in A. | $d_4^{25}$ |
|---|---|---|
| 16·7 | 5·71 | — |
| 33·3 | $5{\cdot}71_4$ | $5{\cdot}3_0$ |
| 42·9 | $5{\cdot}76_0$ | $5{\cdot}2_0$ |
| 50·0 | $5{\cdot}78_7$ | $5{\cdot}1_1$ |
| 66·7 | $5{\cdot}80_4$ | $5{\cdot}0_9$ |
|  | $5{\cdot}81_6$ | — |
| 83·3 | $5{\cdot}84_2$ | $4{\cdot}9_7$ |
| 100·0 | $5{\cdot}87_3$ | — |

An indium phosphide semiconducting cell has been used to determine the intensities of neutron sources.[284]

## Thallium

Claims have been made for the preparation of trithallium phosphide by heating together the correct proportions of thallium and white phosphorus in a sealed tube at 400°C.[285] It is a black compound which decomposes in moist air, ignites if heated in air and reduces potassium permanganate.[285]

In a thermal investigation of the thallium–phosphorus system an unidentified compound was found at 75 atomic-% of phosphorus. This corresponds to thallium triphosphide.[286]

The original phase diagram for the thallium–phosphorus system has been corrected and is shown in Fig. 14.[6]

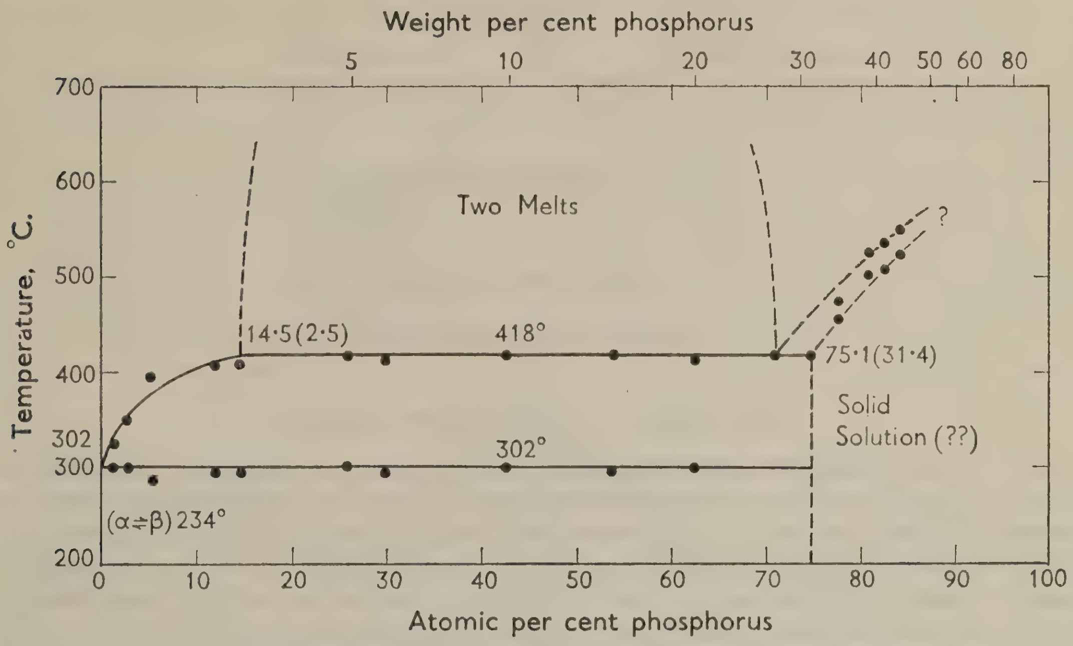

FIG. 14.—Phosphorus–thallium phase diagram

## GROUP 4

### Tin

Brief mention of tritin diphosphide has been made but only of its use as a catalyst in the production of high mol.-wt. polyesters.[287–8]

In an attempt to prepare tin triphosphide a mixture of tin and phosphorus in the ratio 1:3 was cooled slowly *in vacuo* from 700°C.[289] Chemical analysis showed that the product was tin monophosphide. Its crystal structure has hexagonal symmetry with $a = 8{\cdot}78$ A., $c = 5{\cdot}98$ A. The density, calculated from the *X*-ray data, agrees well with the measured density of 5·01 g./c.c. There is no reaction between tin monophosphide and concentrated nitric acid even at 300°C.[289]

Segregation phenomena have been studied in the system tin–phosphorus–gold[97] and the copper corner of the system tin–phosphorus–copper has received some attention, mainly on account of the phosphor bronzes.[84–5, 87–8]

### Lead

No lead phosphides have been prepared but several ternary compounds involving a second metal have been reported.[169, 290] $HgPbP_{14}$, $CdPbP_{14}$ and $ZnPbP_{14}$ were prepared by reaction of an alloy of lead and the appropriate second metal with red phosphorus. The temperature was maintained at 525° to 610°C. for a number of days and silvery coloured materials having high $d$ were obtained. *X*-Ray work showed that the compounds contain parallel zig-zag chains of phosphorus atoms.[290] They do not conduct electricity and are only slightly reactive chemically, being gradually attacked by atmospheric oxygen and not at all by boiling non-oxidizing acids.

## GROUP 5

### Antimony

The systems antimony–phosphorus–iron and antimony–phosphorus have been studied[291] but no phosphides of antimony have been reported. Fig. 15 summarizes the work on the antimony–phosphorus system.[291]

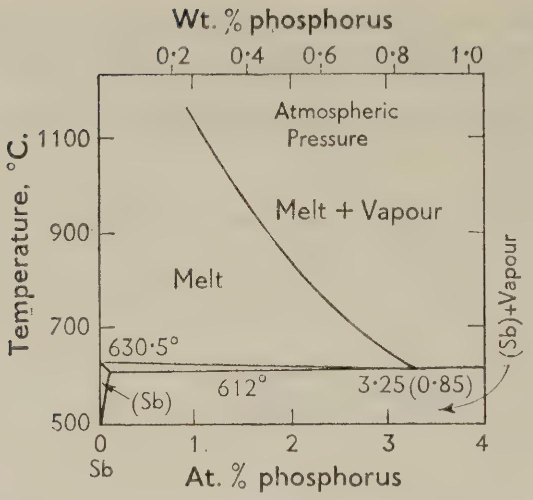

FIG. 15.—Phosphorus–antimony phase diagram

## THE FIRST TRANSITION SERIES

Some of the transition metal phosphides such as those of zirconium, titanium and vanadium are extremely inert, showing no signs of oxidation in air even at 1000°C.[292] Because of their inert nature, the definition of 'hard metals' has been broadened to include them with certain carbides, nitrides, borides and silicides.[293] The structures of many of these phosphides are similar to those of carbides and nitrides. Molybdenum monophosphide is isomorphous with tungsten carbide and as with the 'hard metals' the higher co-ordination number is retained, but the metal atom lattice shows an expansion of approximately 15% as against 5 to 10% for the nitrides and carbides.

*Table VI.—The Crystal Structures of Transition Metal Monophosphides*

| IIIA | IVA | VA | VIA | VIIA | VIIIA | |
|---|---|---|---|---|---|---|
| ScP<br>B1 | TiP<br>Bi | VP<br>B8 | CrP<br>B31 | MnP<br>B31 | FeP<br>B31 | CoP<br>B31 |
| YP<br>B1 | ZrP<br>B1 ← Bi | NbP<br>(Bh) ← NbAs | MoP<br>Bh | | RuP<br>B31 | |
| LaP<br>B1 | HfP<br>Bi | TaP<br>(Bh) ← NbAs | WP<br>B31 | ReP | | |

CeP, PrP, NdP, SmP, GdP, TbP, DyP, HoP, ErP, ThP, UP, PuP all have B1 structure.
Notation of structure types:
B1 = NaCl, B8 = NiAs, B31 = MnP, Bh = WC, Bi = TiP. Arrow points to the structure type which occurs with phosphorus deficiency.

The crystal structures of the transition metal monophosphides have been collated[563] (see Table VI). They are of six different types. The IIIA group, the lanthanide and the actinide monophosphides have an NaCl type lattice. Group IV phosphides have NaCl, TiP or NiAs lattices. Group V (2nd and 3rd period) have a NbAs lattice and a distorted variation tending towards the tungsten carbide type which is fully developed in MoP. The remaining phosphides have MnP or NiAs type lattices.

The monophosphides of Ti, Zr, Hf, Nb, Ta, Mo and W all vaporize by decomposition, yielding phosphorus and a solid phase of lower phosphorus content. In general the thermal stability of transition metal phosphides increases in the order Group VI < Group V < Group IV, and within any one group increases with increasing atomic number,[634] Mo and W being exceptions to the latter rule,[631] as shown by the figures in Table VII.

In the first transition series it is found that compounds of the type $M_3P$ are ferromagnetic if a highly unsaturated atomic shell is connected with a high ratio of lattice constant to atomic shell radius.[294]

*Table VII.—Partial molal free enthalpies of dissociation to* $P_2$[631]

| Compound | Temperature range studied °K. | $\Delta\bar{G}_T^\circ[P_2]$ kcal./mole $P_2$ | | |
|---|---|---|---|---|
| | | 1000°K. | 1500°K. | 2000°K. |
| $TiP_{0\cdot94}$ | 1295–1705 | 55·8 | 40·8 | 25·9 |
| $ZrP_{0\cdot92}$ | 1770–2120 | | 66·9 | 51·1 |
| $NbP_{0\cdot95}$ | 1200–1450 | 55·4 | 34·0 | |
| MoP | 1190–1450 | 54·3 | 28·3 | |
| WP | 950–1250 | 36·7 | 17·3 | |

### Scandium

Scandium monophosphide has been prepared by reaction of scandium filings with red phosphorus in an evacuated quartz tube at 1000°C. It has a cubic (NaCl type) structure with $a = 5{\cdot}312$ A.,[564] 5·302 kx.[630] The calculated density is 3·365 g./c.c. The compound is thermally stable on heating at $10^{-4}$ torr. No polymorphous transformations are found between 20–1500° and the compound does not melt below 2000°. It is oxidized by heating in air, with formation of scandium phosphate. Unaffected by water or bases, it is completely decomposed by dilute mineral acids.

### Titanium

The existence of trititanium monophosphide was indicated in experiments in which dry phosphine in a carrier stream of argon was passed over titanium powder.[295] In other experiments, designed to give dititanium phosphide, and in which titanium was heated with phosphorus, a phase was obtained which *X*-ray methods showed to be isomorphous with tri-iron phosphide,[296, 635] or trivanadium phosphide.[565] In the latter work, the tetragonal lattice was assigned the structure parameters $a = 9{\cdot}956$, $c = 4{\cdot}988$ A. A phase rule study of the titanium–phosphorus system confirmed the existence of trititanium monophosphide, having a tetragonal lattice $a = 9{\cdot}28$, $c = 4{\cdot}99$ A. and melting peritectically at 1760°.[636]

Dititanium phosphide has been prepared by reaction of dry phosphine with titanium at 800°C.[297, 295] If the temperature is allowed to rise above 800°C. there is a tendency for titanium monophosphide to form. Dititanium phosphide, m.p. 1920°, is claimed to be isomorphous with $Fe_2P$, having $a = 6{\cdot}71$, $c = 3{\cdot}46$ A.[636] Other work has shown evidence for a subphosphide which was thought to be dititanium monophosphide,[298, 635] but later investigations have shown that at least one of these compounds was trititanium monophosphide. However, more recently still clear evidence has been obtained for the existence of a new phase, approximating to pentatitanium triphosphide, $Ti_5P_3$ or $TiP_{\sim 0\cdot6}$. This phosphide is formed by the thermal decomposition of titanium monophosphide,[631] by the reaction of titanium tetrahydride with phosphine, or by the interaction of titanium with phosphorus or titanium phosphide.[635] An *X*-ray study of single crystals of $Ti_5P_3$ showed the lattice to be hexagonal, of $Mn_5Si_3$ type with space group $P6_3/mcm$,[632] $a = 7{\cdot}238$, $c = 5{\cdot}088$ A.[633] This phosphide seems to be distinct from trititanium diphosphide, $Ti_3P_2$ (tetragonal, $a = 7{\cdot}48$, $c = 10{\cdot}49$ A., congruent m.p. 2100°) and tetratitanium triphosphide (cubic, $a = 7{\cdot}425$, peritectic m.p. 2060°) observed in a phase rule study of the titanium–phosphorus system.[636] The latter phosphide may be identical with the phase of composition $TiP_{0\cdot7}$–$TiP_{0\cdot9}$ detected in another study.[635]

As indicated above, titanium monophosphide is formed when phosphine is passed over powdered titanium at a temperature higher than 800°, preferably 850°C.[295, 299] Other studies, in which phosphides were made by direct reaction of the elements, by reaction of tricalcium diphosphide with titanium metal,[566] or by reaction of phosphine with titanium tetrachloride, indicate that a homogeneous phase $TiP_{0\cdot94}$ exists.[298, 292] This is a grey-black metallic compound with *d* 3·95 g./c.c.[298] (4·08 g./c.c.[292]). It is very stable to heat, having no appreciable v.p. of phosphorus even at 1100°C.[298] The enthalpy of formation of titanium monophosphide, determined from heats of combustion, is −63·4 kcal./mole.[300] $TiP_{0\cdot94}$ is attacked only slightly by acids and water at room temperature[298, 292] whilst titanium monophosphide is highly resistant to oxidation.[299]

The diphosphide of titanium can be obtained by heating together titanium powder and red phosphorus or by heating the metal powder in a stream of phosphine and hydrogen.[292] It is orthorhombic, with $a=6{\cdot}181$, $b=8{\cdot}256$, $c=3{\cdot}346$ A.[637]

Crystal structure studies have been carried out on the ternary systems Ti(Cr, Mo or W)P,[638] TiCoP and TiFeP,[653] a compound which had been reported earlier.[462]

### Vanadium

By heating powdered vanadium with red phosphorus for several days at between 400°C. and 1000°C. a semimetallic grey black trivanadium phosphide with *d* 5·46 g./c.c. and molecular volume 11·33 c.c. is obtained which is attacked by concentrated sulphuric acid and warm nitric acid.[301] The compound forms tetragonal crystals isomorphous with $Ti_3P$, having $a=9{\cdot}387$, $c=4{\cdot}756$ A.[565]

Divanadium phosphide has been reported as being formed when a fused mixture consisting of $Li_3PO_4+\frac{1}{10}V_2O_5+2LiF$ is electrolyzed at 900°C. at 25 amp. and 5 volts.[302, 9] This compound is thought by others to be a mixture of monovanadium phosphide and divanadium trioxide.[301] An *X*-ray investigation lends a slight amount of support to this view because a phosphide lower than the monophosphide could not be confirmed.[292] However the compound crystallizes in metallic needles having *d* 4·5 g./c.c. It is readily attacked by boiling sulphuric acid, hot nitric acid, and boiling aqueous potassium persulphate but not concentrated hydrochloric acid. Solutions of alkali have no effect on it but fused alkali metal carbonate, nitrate or persulphate forms vanadates and phosphates.[302] Divanadium phosphide is an active catalyst for the decomposition of ammonia.[303]

Electrolysis of fused alkaline phosphate melts containing vanadium oxide[302, 9, 304] produces vanadium monophosphide, VP, as does heating powdered vanadium with red phosphorus for several days at elevated temperatures,[301] or causing tricalcium diphosphide to react with vanadium metal or chloride.[566] It is a grey-black compound, the density of which is variously reported as being 4·0 g./c.c.,[302] 4·69 g./c.c.[301] and 4·72 g./c.c.[292] The molecular volume is 17·7 c.c.[301] *X*-Ray powder photographs of vanadium monophosphide resemble those of molybdenum monophosphide but not those of the corresponding tantalum and niobium compounds.[301] As with other phosphides of vanadium, it is not attacked by water or dilute acid at room temperature, forms vanadates and phosphates with fused alkali, and reacts with warm nitric acid or concentrated sulphuric acid.[301–2, 292] Vanadium monophosphide reacts slowly with white phosphorus to form the diphosphide.[301]

The diphosphide is conveniently prepared from the powdered metal by heating it with red phosphorus[301, 292] or by passing a mixture of phosphine and hydrogen over it.[292] It is a black compound having *d* 4·5 g./c.c.[302] From the tensimetric analysis shown in Fig. 16,[301] a value of 57 kcal. was calculated for the heat of decomposition of vanadium diphosphide according to equation (23):

$$4VP_2(s) \rightarrow 4VP(s) + P_4(g) \tag{23}$$

The compound is probably isomorphous with the corresponding phosphides of tantalum and niobium since the *X*-ray diagrams are similar.[301] It is attacked by oxidizing acids.[301]

Phosphides of vanadium have been compared with those of tantalum and niobium[305] and a patent for their manufacture by heating finely divided metal with a large excess of phosphorus in a sealed container has been granted.[306]

The vanadium–phosphorus–iron system has been partly investigated.[307–8]

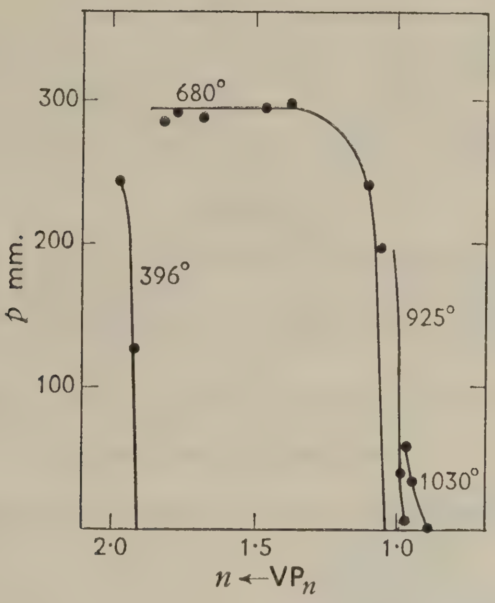

FIG. 16.—Vapour pressure analysis of the $VP_2$/VP system

## Chromium

Trichromium phosphide has been recognized in several phase studies[292, 309–10, 91] and has been obtained in mixtures by the electrolysis of fused salts.[311–2] It is isomorphous with the corresponding manganese, iron and nickel phosphides[309, 292] and forms continuous solid solutions with iron and nickel phosphides.[310, 91] The compound is a greyish black substance which melts incongruently. Its unit cell dimensions are $a = 9{\cdot}186$ A. and $c = 4{\cdot}558$ A.[308] and it has $d$ 6·25 g./c.c.[292] Water and dilute acids do not affect it at room temperature.[292]

Dichromium phosphide is formed together with monochromium phosphide when chromium phosphate is heated in hydrogen at 600°C. with continuous removal of the water vapour formed.[43] It has also been recognized in various phase studies.[91, 310] Dimanganese phosphide will only dissolve 50 molar-% of dichromium phosphide, whereas the iron and nickel compounds form continuous series of solid solutions.[91] Phase studies (see Fig. 17) showed the presence of this compound in the chromium–phosphorus system[310] but other investigators using $X$-ray methods were unable to identify it.[309]

Monochromium phosphide is prepared by electrolysis of fused alkali metal salts containing chromium salts[10] and, as indicated above, it is formed together with other phosphides when chromium phosphate is reduced with hydrogen.[43] When the diphosphide is heated with metal powder in a sealed silica tube it is converted into the monophosphide,[292] whilst the straightforward method of heating red phosphorus with chromium in a silica tube has been used successfully.[313] The reaction of tricalcium diphosphide with chromium metal or chloride is also said to yield chromium monophosphide.[566] Finally, phosphine passed over powdered chromium heated at 850°C. forms monochromium phosphide in 6 hr.[314, 299] The compound which is greyish black with a metallic lustre[292] and has $d$ 5·25 g./c.c.[292] crystallizes with the MnP type structure with $a = 5{\cdot}362$, $b = 3{\cdot}113$, $c = 6{\cdot}018$ A.[313] Isomorphism with the manganese, iron, and cobalt compounds has been established.[309, 292, 639] From measurements in a tensimetric analysis, shown in Fig. 18, the investigators were able

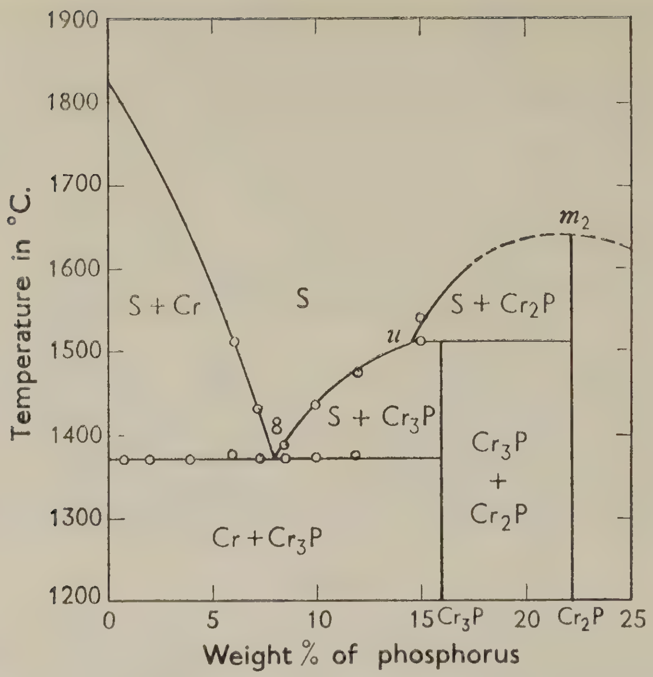

FIG. 17.—The phase diagram of chromium and phosphorus

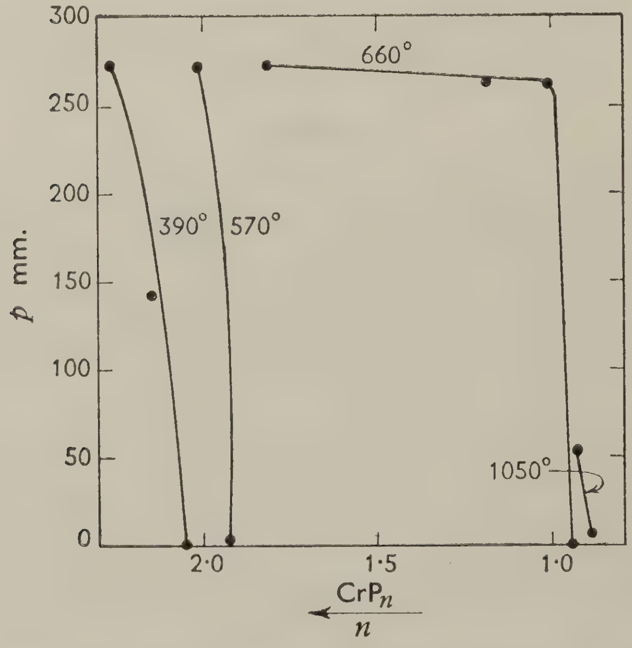

FIG. 18.—Vapour pressure analysis of the chromium–phosphorus system

to calculate a heat of reaction of monochromium phosphide with phosphorus according to equation (24)[315]:

$$(24) \qquad CrP(s) + P(white) \rightarrow CrP_2(s) \qquad \Delta H = -6{\cdot}5 \text{ kcal./mole}$$

Monochromium phosphide is highly resistant to oxidation,[299] and is not attacked by water or dilute acids at room temperature.[292, 314] It has been shown to be active as a catalyst for the decomposition of ammonia.[303]

If the metal powder is heated with red phosphorus or if a dry mixture of phosphine and hydrogen is passed over the metal powder heated to between 700° and 900°C. for between 2 and 10 hr., the diphosphide is obtained.[292] The data used to obtain the heat of reaction of monochromium phosphide can also give the heat of decomposition of chromium diphosphide according to equation (25)[315]:

$$(25) \qquad 4CrP_2(s) \rightarrow 4CrP(s) + P_4(g) \qquad \Delta H = +39 \pm 3 \text{ kcal.}$$

This phosphide has been used as a protective coating for metals which are readily oxidized.[316]

Ternary systems investigated include the chromium–phosphorus–manganese, chromium–phosphorus–nickel, chromium–phosphorus–copper, chromium–phosphorus–iron systems[91, 310] and the chromium–phosphorus–boron system.[344] The nickel-containing system is characterized by a ternary sigma phase.[308] In the boron system it was shown that the solid solubility of boron in $Cr_3P$ is appreciable.[344]

## Manganese

The manganese–phosphorus phase diagram was investigated up to 45 atomic-% of phosphorus. The results of this work are shown in Fig. 19 where it can be seen that a tetramanganese phosphide phase was claimed to exist.[317]

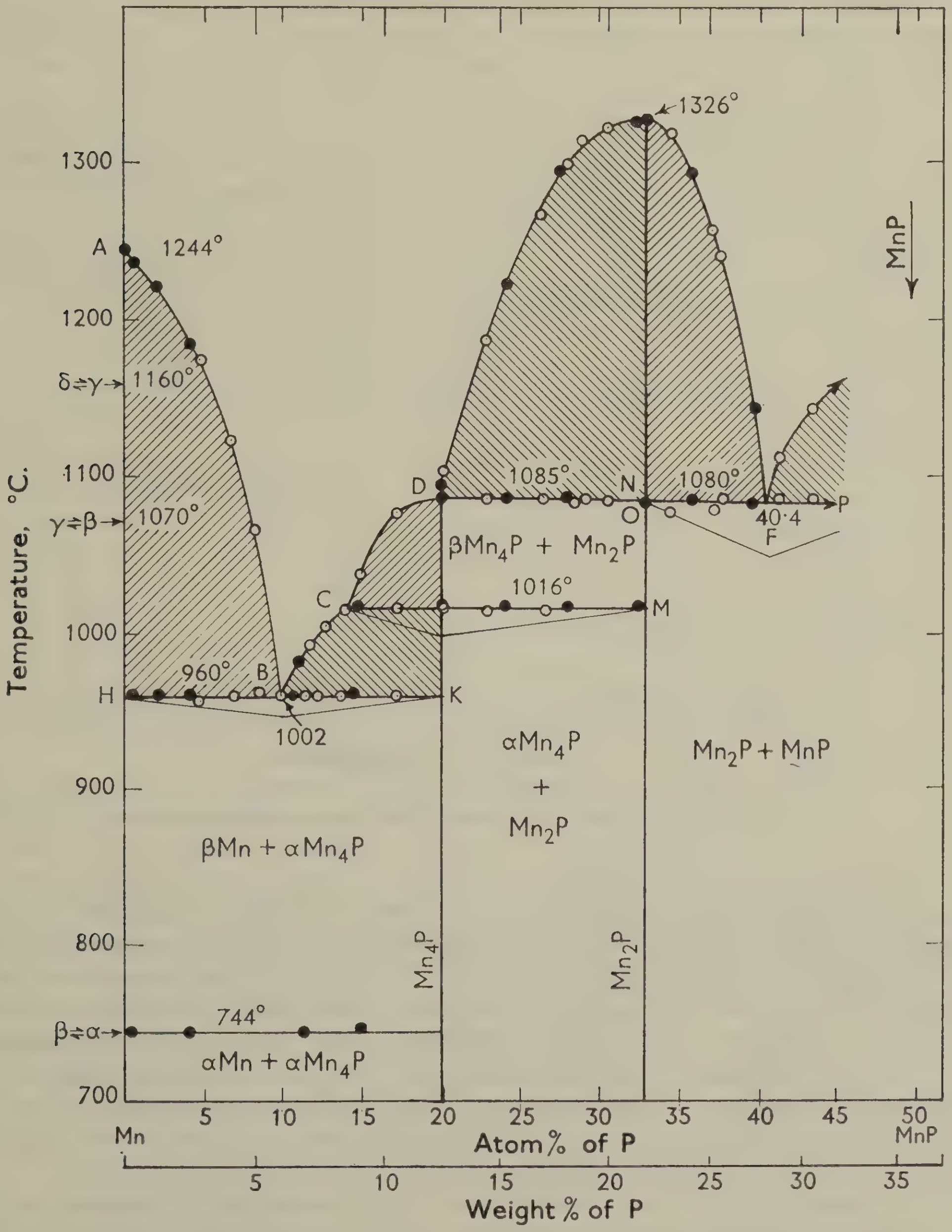

FIG. 19.—Phase diagram of the Mn–MnP system

Repetition of this work[318] (Fig. 20) suggests that the manganese-rich phase is trimanganese phosphide. This has been confirmed by $X$-ray work which disclosed a new phase, trimanganese phosphide but not tetramanganese phosphide.[319] The $X$-ray measurements give the space group as being probably $S_4^2$ because of isomorphism with tri-iron phosphide.[319] This has been confirmed[320] and the unit cell dimensions are variously given as $a=9{\cdot}160$, $c=4{\cdot}599$ A.,[319] $a=9{\cdot}00$, $c=4{\cdot}57$ A.[318] and $a=9{\cdot}181$, $c=4{\cdot}568$ A.[320] Although it is isomorphous with the corresponding iron compound, it forms a continuous series of solid solutions only with trichromium phosphide.[319]

Electrolysis of fused alkali metal phosphate melts containing manganese salts,[10, 9, 321, 311–2] and reduction of trimanganese phosphate with hydrogen[43] have both yielded dimanganese phosphide. The crystal structure has hexagonal symmetry, space group $P\bar{6}2m$, with $a=6{\cdot}08$, $c=3{\cdot}45$ A.[322] or $a=6{\cdot}081$, $c=3{\cdot}460$ A.[320] A Curie temperature of 20°C. for ferromagnetism in this compound has been reported,[294] but other work has shown that dimanganese phosphide is not ferromagnetic and that any ferromagnetism must be due to monomanganese phosphide.[323] There are indications from $X$-ray work that dimanganese phosphide may have a finite homogeneity range.[320] Galvanomagnetic measurements on material containing both monomanganese phosphide and dimanganese phosphide show that the Hall effect varies linearly with magnetization near the Curie point. The Hall constant decreases with decreasing temperature which indicates metallic type conduction.[324–5]

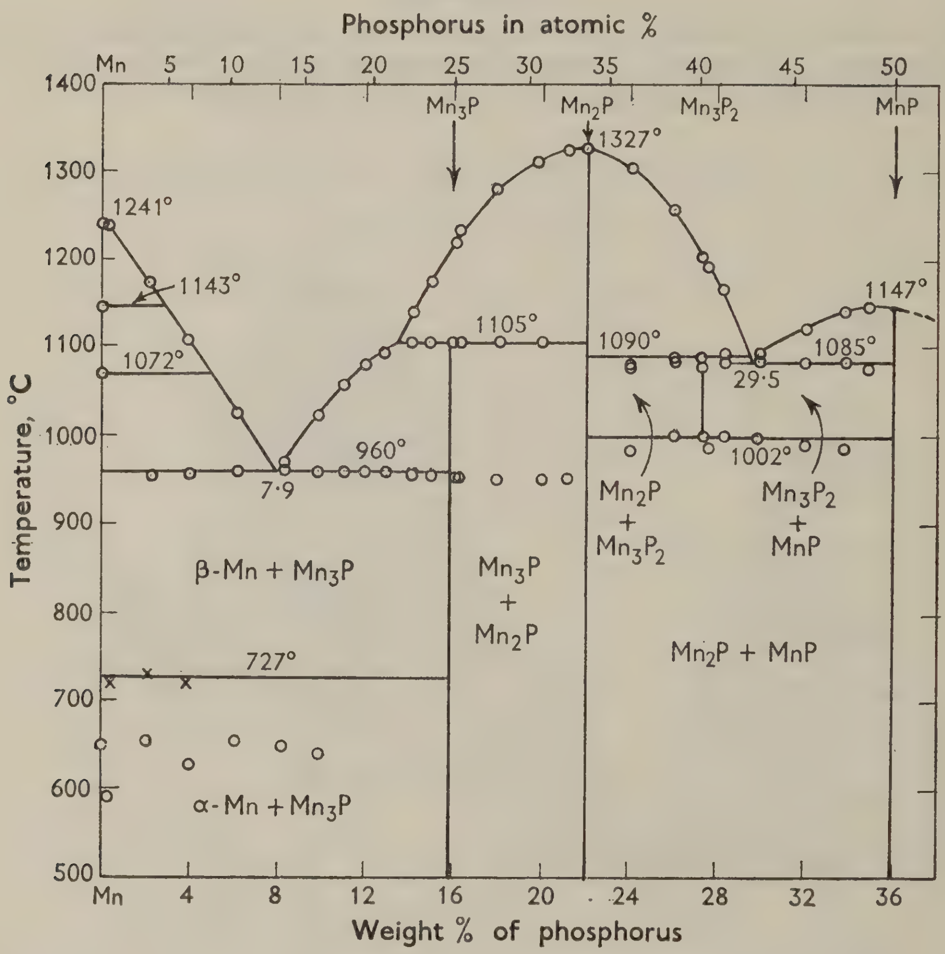

FIG. 20.—Part of the manganese–phosphorus phase diagram

Besides disagreeing as to the composition of the manganese-rich phase, the phase studies shown in Figs. 19 and 20 also disagree concerning the existence of the compound trimanganese diphosphide. It is reported as being ferromagnetic and to decompose at 1090°C. to give dimanganese phosphide and monomanganese phosphide.[318] *X*-Ray powder work on the manganese–phosphorus system throws doubt on the existence of this compound.[320]

The well-known method of electrolyzing fused phosphate melts containing salts of the metal has been used as a means of preparing monomanganese phosphide.[10, 9, 321, 311–2] In a study of the magneto-calorie effect,[326] monomanganese phosphide was prepared by reaction of a powdered mixture of red phosphorus and vacuum distilled electrolytic manganese at 650°C. for 50 hr. in a sealed evacuated quartz tube.[327–8] Variations of the technique have also been used.[313, 329] Finally, the reaction of tricalcium diphosphide with manganese metal or halide is said to give the monophosphide.[566] The monophosphide is magnetic, has $d$ 5·6 g./c.c.[321] and an orthorhombic crystal structure with $a=3{\cdot}167$, $b=5{\cdot}905$, $c=5{\cdot}249$ A.[322] or $a=5{\cdot}258$, $b=3{\cdot}172$, $c=5{\cdot}918$ A.,[313] or $a=5{\cdot}9$, $b=5{\cdot}25$, $c=3{\cdot}16$ A.[329] The orthorhombic B31 structure is distorted from a hexagonal nickel arsenide (B81) structure, due to metal–metal bonding in the hexagonal basal planes.[640] Manganese monophosphide is isomorphous with chromium, iron and cobalt monophosphides.[639]

Several investigations into its electrical and magnetic behaviour have been made. Magnetic moment measurements indicate a moment of 14·1 Weiss magnetons[330] and 1 Bohr magneton.[331] This last value has been explained by advancing the hypothesis that consecutive planes of manganese atoms in the structure are in states $3d^5$, $4s^2$ or $3d^7$. The assumption of an antiferromagnetism mechanism in this compound could not be confirmed.[332, 641] A value of $5{\cdot}98 \pm 0{\cdot}15$ Weiss magnetons, obtained from measurements of specific magnetization versus temperature and field strength,[333] agrees more with that of Guillard[331] than with that of Foex.[330] A large variation of Curie point was observed in these experiments but other workers have given the Curie point as 22°C.,[334, 327–8] 20°C.,[335] 25°C.,[333, 336] $18{\cdot}3 \pm 0{\cdot}2$°C.[641] and 40°C.[337] The value of 40°C. probably refers to the paramagnetic Curie temperature since a value of 39°C. has been reported.[336] Temperature versus resistance plots, which are very nearly linear above and below the Curie point, gave breaks at 22°C.[324, 338] The Curie temperature is independent of the intensity of the magnetic field.[325] Monomanganese phosphide is strongly paramagnetic above its critical temperature.[337] Measurements of volume change, magnetic transitions and density transitions[323] in going from the ferromagnetic to the paramagnetic state exhibit no hysteresis effects. This has been taken to indicate that the temperature at which spontaneous magnetization becomes zero is lower than the temperature of zero susceptibility.[339] Specific heat measurements in the neighbourhood of the critical temperature have been made[328, 340] and show a small increase of the order expected from the Weiss theory, but the accuracy of measurement was not high enough to decide whether the maximum in the specific heat corresponded to the maximum value of $I\partial I/\partial T$ or $\partial I/\partial T$ ($I$ is the saturation magnetic intensity).[340] The anomaly in the specific heat has a maximum value at 17°C. and then decreases up to 30°C.[328] Electric and galvanomagnetic measurements have been made[325, 324] and indicate that the conduction of monomanganese phosphide is governed by the overlap of the $d$ shells of the manganese atoms forming a narrow $d$ conduction band. The concentration of carriers is high and is comparable with that in metals.[325] The Hall effect near the Curie point varies linearly with magnetization and the Hall constant decreases with decreasing temperature.[324] Calculations on the filling of Brillouin zones and consideration of chemical binding between atoms has led to the prediction of semiconductor properties.[341]

Monomanganese phosphide is grey with a metallic lustre[342] and shows complete solid solubility in monocobalt phosphide.[313] The heat of combustion, −270 kcal./mole and heat of formation, −23 kcal./mole have been determined.[329] It is not attacked by cold water, cold dilute acids or cold concentrated nitric acid. It is attacked, however, by hot dilute nitric acid, molten alkali, alkali metal salts, disodium oxide and lead dioxide.[321] The compound is active as a catalyst for the decomposition of ammonia.[303]

The reaction of powdered manganese and red phosphorus in a heated sealed tube has been used as a method for preparing manganese triphosphide. V.p. measure-

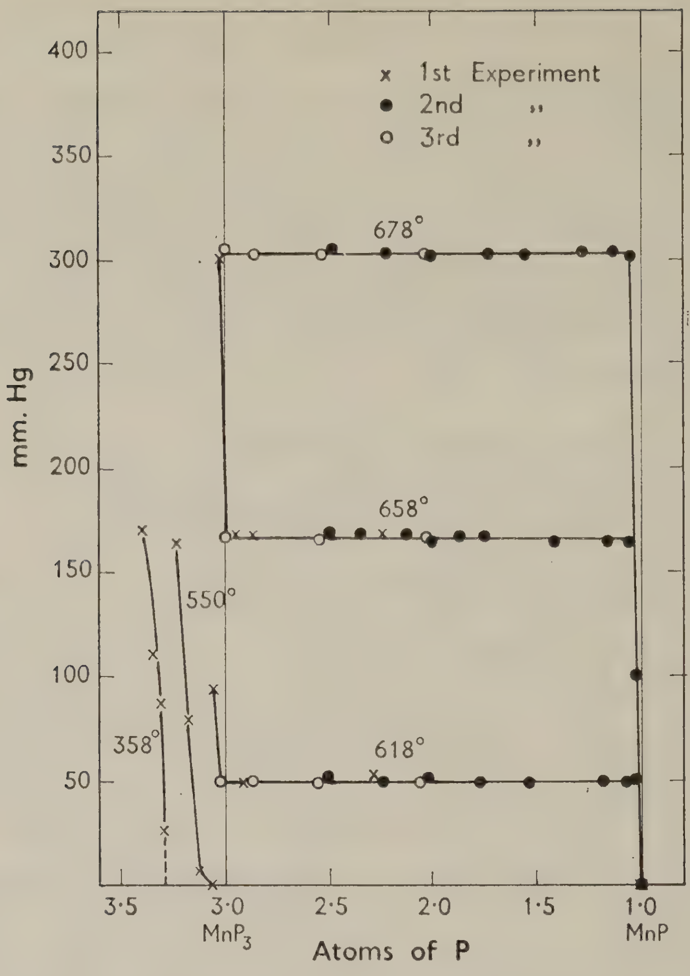

FIG. 21.—Vapour pressure analysis in the manganese–phosphorus system

ments on some preparations are shown in Fig. 21. From these results the dissociation pressure was shown to obey equation (26):

$$(26) \qquad \log p_{(\mathrm{mm.})} = -11856/T + 14{\cdot}948$$

and the heat of dissociation was calculated for equation (27):

$$(27) \qquad 2\mathrm{MnP_3(s)} \rightarrow 2\mathrm{MnP(s)} + \mathrm{P_4(g)} \qquad \Delta H = +54{\cdot}2 \text{ kcal.}$$

Manganese triphosphide takes up phosphorus into solid solution.[342]

Manganese forms a series of ternary phosphides of general formula $Li_{8-x}Mn_xP_4$. These can be obtained by heating trilithium phosphide, manganese and phosphorus at 800°C. in argon. They have been discussed under lithium and Table II (page 292) lists some of their properties.[29]

Ternary systems manganese–phosphorus–chromium,[91] manganese–phosphorus–iron,[91, 343] manganese–phosphorus–nickel[91] and manganese–phosphorus–boron[344] have been investigated. In the last system a ternary phase $Mn_5PB_2$ exists which is isostructural with $Fe_5PB_2$ and $Co_5PB_2$.[344]

## Iron

Andrieux's method, i.e. electrolysis of fused alkali metal phosphates containing a compound of the metal of which it is required to prepare the phosphide, has been applied to the synthesis of tri-iron phosphide.[345, 9] In this reaction the phosphide produced depends upon the molar ratio of ferric oxide to phosphorus pentoxide present in the melt and Fig. 22 shows the ratios at which various iron phosphides are produced. Thermal and tensimetric analysis served to identify the compounds formed.[9] Reaction of the elements in a heated sealed quartz tube produces tri-iron phosphide together with higher phosphides.[346, 50] For some magnetic measurements it has been produced by fusion of the elements,[347] whilst reduction of $Fe_2O_3$–$FePO_4$ preparations with hydrogen or carbon monoxide also produces tri-iron phosphide, though other phosphides may also be produced depending upon the ratio of iron to phosphorus in the original oxide–phosphate preparation.[348] *X*-Ray powder methods have been used to identify this phosphide in a study of the iron–phosphorus system,[349–51] and in an unknown spherulitic phase present in some tektites.[567] Other *X*-ray work has confirmed previous investigations and shown that the crystal structure is tetragonal with $a = 9{\cdot}090$, $c = 4{\cdot}446$ A.[352] Tri-iron phosphide has *d* 7·11 g./c.c.,[346] 7·13 g./c.c.[347] and its heat of formation (shown with those of other iron phosphides in Fig. 23) is −35·2 kcal./mole.[50] The free energy of formation of solid $Fe_3P$ from the gaseous elements has been estimated as $-50{,}600 + 11{\cdot}3T$ g.-cal./mole over the range $T = 298$–1439°K.[548] Magnetic measurements give for this compound a Curie temperature of 443°C. and a saturation moment of $1{\cdot}84\mu_B$ per atom of iron.[347] The maximum coercive field of 107 oersted was observed at 18°C.[347] Tri-iron phosphide can be separated from di-iron phosphide by magnetic means.[353] It has been recognized as a precipitation phase from solid solution of phosphorus in α-iron[354]

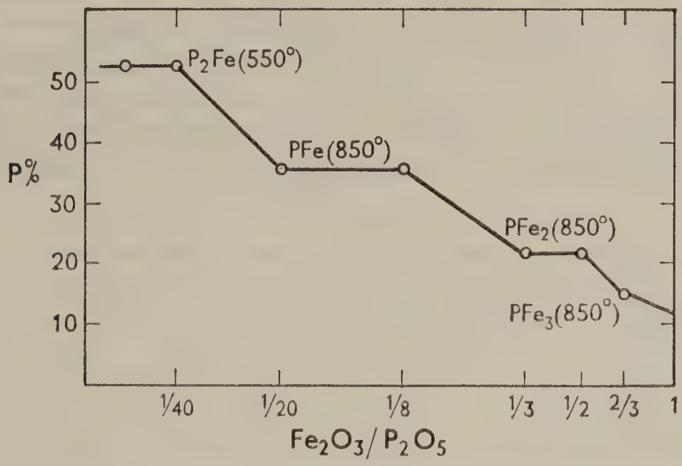

FIG. 22.—The iron phosphides formed at different $Fe_2O_3/P_2O_5$ ratios

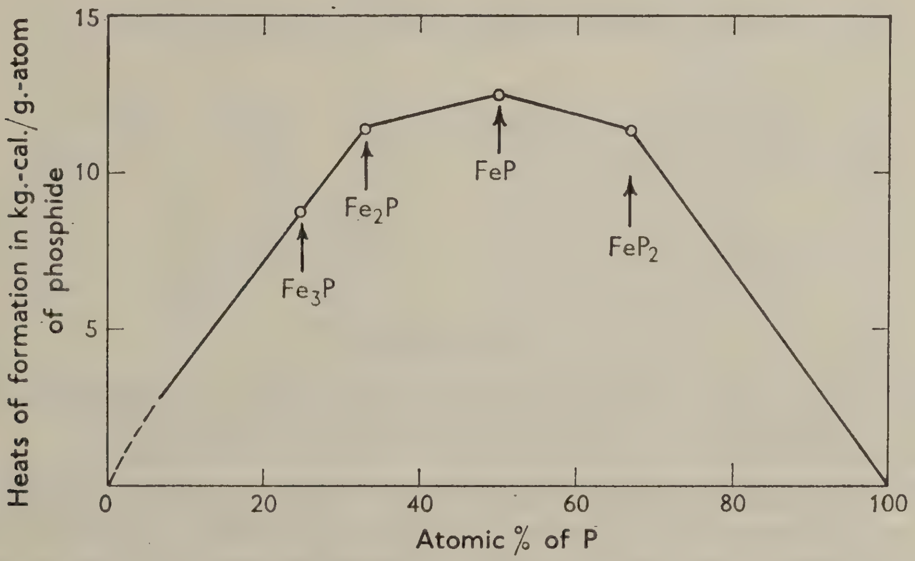

FIG. 23.—Heats of formation in the iron–phosphorus system

and the habit plane of this precipitated phase has been predicted using the theory of martensitic transformations.[355] This phosphide is not very resistant to chemical attack, being oxidized in the atmosphere and dissolved by acids.[345] Solid state reactions between lime, oxygen and tri-iron phosphide have been shown to proceed according to equation (28)[356]:

$$3CaO + 2Fe_3P + 7O_2 \rightarrow Ca_3(PO_4)_2 + 3Fe_2O_3 \quad (28)$$

Di-iron phosphide has been prepared by Andrieux's method,[9, 345, 10] by heating the elements together in a sealed evacuated quartz tube,[346] and by heating iron phosphates in an atmosphere of hydrogen or carbon monoxide above 950°C.[357, 348] A study of the iron–phosphorus system[349–50] as well as the iron–phosphorus–nickel system[358] showed the existence of di-iron phosphide. Further evidence is provided by the existence of discontinuities at above 22% P in the magnetic susceptibility,[642] density and surface tension[643] isotherms for the iron–phosphorus system. The manufacture has been accomplished by adding electrolytic iron to a molten copper–phosphorus alloy.[359] *X*-Ray work has shown that the crystal structure is hexagonal with $a=5{\cdot}87$, $c=3{\cdot}45$ A.,[359] $a=5{\cdot}852$, $c=3{\cdot}453$ A.,[360] $d=6{\cdot}89$ g./c.c.,[359] 6·77 g./c.c.[346] V.p. measurements are shown in Fig. 24.[346] The heat of formation has been variously given as −34·5 kcal./mole,[50] −35·2 ± 2 kcal./mole at 900°K. and −41·0 ± 4·1 kcal./mole.[361] At 1350°C. the heat of dissociation to $P_2$ vapour is 111·2 ± 2 kcal./mole.[568] The estimated free energy of formation of solid $Fe_2P$ from the gaseous elements over the temperature range 298–1638°K. is given by $\Delta G = -49{,}900 + 11{\cdot}3T$ g.-cal./mole.[548]

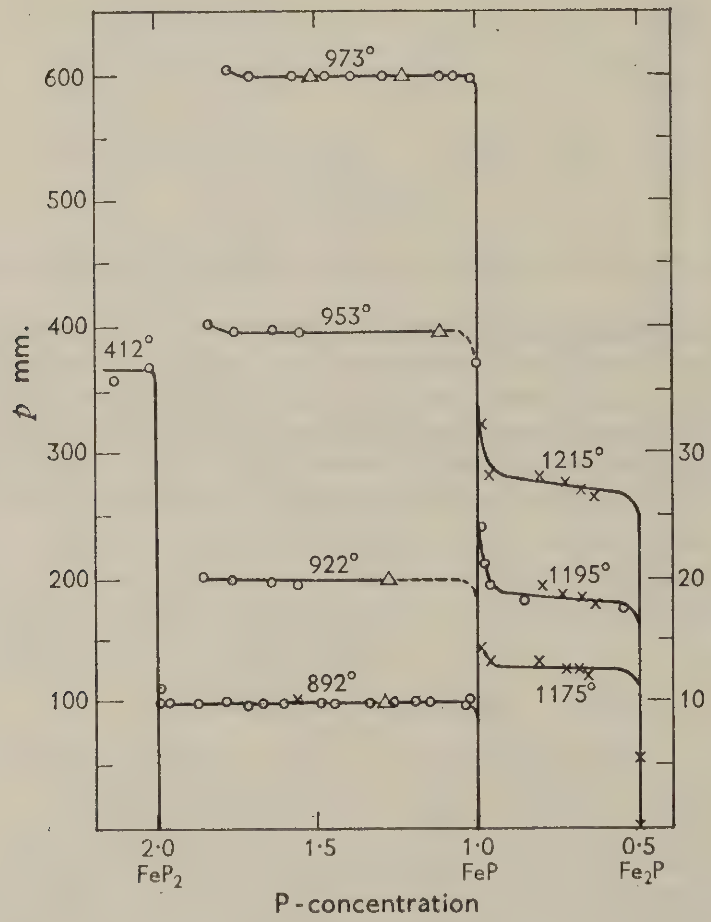

FIG. 24.—Vapour pressure analysis of iron phosphides. The right hand pressure scale corresponds to the determinations at 1175, 1195 and 1215°C.

Magnetic measurements have shown that di-iron phosphide, with the magnetization vector along the axis of symmetry of the hexagonal net, has a Curie point of

$-7$°C. and an absolute moment of 1·32 Bohr magnetons per atom of iron.[362] Samples containing a slight excess of phosphorus appeared to possess extreme magnetic hardness[362]; (magnetically hard materials retain a considerable portion of the magnetic moment they acquire on magnetization after the magnetizing field has been removed). Other workers have shown that the extrapolated saturation magnetization reaches a value at 0°C. of 66·3 gauss/g. of iron, a value which corresponds to a spin moment of $0{\cdot}85 \pm 0{\cdot}02$ Bohr magneton per iron atom.[363] It was also shown that the Curie–Weiss law[326] holds up to 900°K. and Curie points were observed at 306°K. (ferromagnetic) and 478°K. (paramagnetic).[363] A total magnetic moment of 14 Weiss magnetons corresponds with a neutral iron atom.[330]

Deposition studies have shown that this compound can be deposited electrolytically on a wire such that the [0001] axis is perpendicular to the surface of the wire.[364] It has been investigated as a material suitable for corrosion-resistant electrodes. Current–voltage curves were plotted in acids, alkalis and saturated potassium chloride solutions whilst rates of corrosion by hydrochloric acid, sulphuric acid, nitric acid and potassium hydroxide were determined at 25°C. and 80°C.[365] The same workers showed that this compound is a good conductor of electricity and has a negative coefficient of resistivity.[365] When used as an anode in normal sulphuric acid, normal potassium hydroxide, saturated potassium chloride and normal potassium acetate–normal acetic acid solution, di-iron phosphide is oxidized to ferric and orthophosphate ions.[365] Disproportionation of carbon monoxide on this phosphide has been shown to be due to ferric oxide impurity, the phosphide itself being inactive.[366] It was also shown to be inactive as a catalyst in the hydrogenation of *cyclo*hexene.[367] Reactions of di-iron phosphide with oxides FeO, $Fe_2O_3$, MnO, PbO, CaO + FeO, $CaO + Fe_2O_3$ have been examined thermally and heats of reaction shown to differ widely from values calculated using known heats of formation of compounds in each particular case. The differences may possibly be explained by assuming a specific heat effect, because the heats of reaction were studied at high temperatures whereas the calculated heats of reaction apply to normal temperatures.[368] With $Ni_2P$ di-iron phosphide forms single phase alloys.[311]

Monoiron phosphide is produced together with other phosphides when the metal reacts with red phosphorus at high temperatures in a sealed evacuated tube[346] or in an inert atmosphere of argon over the melt.[313] As shown in Fig. 22, it is also produced when sodium phosphate melts containing the correct molar ratio of ferric oxide to phosphorus pentoxide are electrolyzed.[10, 9, 345, 369–70] Iron pyrophosphate can be reduced by hydrogen at 620°C. to yield monoiron phosphide.[43] *X*-Ray investigation has shown that this steel-grey compound has a similar structure to the manganese and cobalt monophosphides. It is orthorhombic with $a = 5{\cdot}782$, $b = 5{\cdot}177$, $c = 3{\cdot}089$ Å.[322] or $a = 5{\cdot}191$, $b = 3{\cdot}099$, $c = 5{\cdot}792$ Å.[313] Two density determinations agree well giving $d = 6{\cdot}0$ g./c.c.[369–70] and $d = 6{\cdot}07$ g./c.c.[346] Its corrosion resistance when used as electrodes has been investigated: similar measurements were made to those given for di-iron phosphide,[365] and like that compound it was oxidized to ferric and orthophosphate ions.[365] The same workers report that it is a good conductor of electricity. Monoiron phosphide has a Curie point of $-58$°C., and an absolute moment of $0{\cdot}36\mu_B$ per atom of iron.[577] The paramagnetic susceptibilities of compositions in the FeP region have been determined.[644] Thermodynamic data are summarized in Fig. 23,[50] Fig. 24[346] and equation (29)[346]:

$$(29) \qquad 4FeP(s) \rightarrow 2Fe_2P(s) + P_2(g) \qquad \Delta H = +72 \text{ kcal.} \qquad t = 1200°\text{C.}$$

More recent values for the heat and entropy of dissociation/mole $P_2$ vapour at 1250°C. ($\Delta H^\circ_{1250} = 84{\cdot}8 \pm 2$ kcal., $\Delta S^\circ_{1250} = 50{\cdot}3 \pm 1$ g.-cal./mole/degree) lead to a value for the heat of formation of FeP (from solid Fe and red P at 900°K.) of $-28{\cdot}6 \pm 2$ kcal./mole.[568] The free energy of formation of solid FeP from the gaseous elements at $T$°K. is given by $\Delta G = -40{,}400 + 11{\cdot}3T$ g.-cal./mole.[548]

Like di-iron phosphide, this compound has been shown to be inactive as a catalyst for the hydrogenation of *cyclo*hexene[367] and for the disproportionation of carbon monoxide[366] but active for the decomposition of ammonia.[303]

It is more resistant to chemical attack than the lower phosphides since it is attacked only slowly by acids, alkalis and aqua regia. Sodium persulphate and boiling concentrated sulphuric acid attack it quite readily.[369] Silicon shows considerable solubility in monoiron phosphide, whilst monocobalt phosphide shows complete solid solubility.[313]

Iron diphosphide, which is the highest phosphide of iron so far prepared, has been obtained by reaction of the elements in a sealed evacuated tube[346, 371] and by Andrieux's method.[345, 10, 9] Results of vapour pressure measurements are shown in Fig. 24 and from these the heat of decomposition according to equation (30) was calculated to be +66 kcal.[346]

$$(30) \qquad 4FeP_2(s) \rightarrow 4FeP(s) + P_4(g) \qquad \Delta H = +66 \text{ kcal.} \qquad t = 930°\text{C.}$$

A more recent determination of the heat and entropy of dissociation/mole $P_2$ vapour at 1000°C. ($\Delta H^\circ_{1000} = 70{\cdot}6 \pm 2$ kcal., $\Delta S^\circ_{1000} = 52{\cdot}9 \pm 1$ g.-cal./mole/degree) leads to a value of $-43{\cdot}6 \pm 4$ kcal./mole for the heat of formation of $FeP_2$ from solid iron and red phosphorus at 900°K.[568] The free energy of formation of solid $FeP_2$ from the gaseous elements at $T$°K. is calculated to be $\Delta G = -64{,}800 + 22{\cdot}5T$ g.-cal./mole.[548]

Its crystal structure is of the marcasite type with $a = 2{\cdot}72(5)$, $b = 4{\cdot}97(5)$, $c = 5{\cdot}65(7)$ Å., $d = 5{\cdot}07$ g./c.c. and molecular volume 23·3 c.c.[346, 645] Iron diphosphide is rather more inert to chemical attack than the other iron phosphides.[345] It is antiferromagnetic.[577]

*X*-Ray studies failed to establish the existence of a phosphide $FeP_3$ which would correspond to $MnP_3$, $CoP_3$ or $NiP_3$.[371]

Individual iron phosphides are not manufactured for any specific purpose although a patent for their use in friction elements for brake linings and clutches has appeared,[75] but a mixture of the di-iron phosphide and the monoiron phosphide (containing approximately 25% of phosphorus) has received a great deal of attention. Ferrophosphorus, as this product is known, is sometimes manufactured for use in special steels and the patent literature on this substance is extensive.[372–82]

In phosphorus production where a phosphate rock is reduced by heating with carbon, some of the phosphorus is lost by combination with iron in the furnace charge to form ferrophosphorus. Efforts have been made to convert this into a useful source of phosphorus. These have included attempts to recover the phosphorus as such,[383–4] whilst other investigations have aimed at producing phosphates which would be useful as additions to animal feed or fertilizers.[385–92] Reaction with sodium sulphate and sodium carbonate at 700°C. gives trisodium phosphate.[393] In air oxidations the product varies according to the temperature of reaction. At 1250°C. the main product is $2Fe_3O_4, 1{\cdot}5P_2O_5$ and the heat of reaction for 1 mole or 142·7 g. of $Fe_2P$ is $-347$ kcal. whilst at lower temperatures the main product is $3Fe_2O_3, 1{\cdot}5P_2O_5$ and the heat of reaction for 1 mole is $-364$ kcal.[394] Oxidation with water vapour occurs starting at a temperature approximately 100°C. higher than air oxidations which produce the same products. For the reaction

$$3Fe_2P + 15{\cdot}5H_2O \rightarrow 2Fe_3O_4, 1{\cdot}5P_2O_5 + 15{\cdot}5H_2$$

the heat of reaction is $-37$ kcal./mole. A second decomposition with alkali metal sulphide or soda solution under pressure or with ammonia plus carbon dioxide can be carried out to give water-soluble phosphates.[394] Chlorine in the nascent state at 400° to 450°C. produced chlorides, the heat of reaction for 1 mole of $Fe_2P$ being $-231$ kcal. Chlorides are produced similarly with phosgene and here the heat of reaction is $-112$ kcal. per mole of $Fe_2P$.[394] In decompositions with nitric acid the best results are obtained with acid at a concentration of 30% which give as products ferric nitrate and phosphoric acid and a heat of reaction of $-573$ kcal./mole $Fe_2P$. This reaction cannot be considered as a means for obtaining phosphoric acid because of the difficulty of removing the iron.[394] However with concentrated sulphuric acid the iron is precipitated as anhydrous ferrous sulphate but even here it may be necessary to employ oleum to maintain anhydrous conditions.[394] Above 300°C.

aqueous alkali with or without the addition of oxygen reacts completely with ferrophosphorus. In reactions without the addition of oxygen hydrated FeO and $Fe_2O_3$ are obtained, whilst with added oxygen $Fe(OH)_3$ is the reaction product. Alkali metal carbonates react to a lesser extent than alkali metal hydroxides. Fusion at 1000°C. with sodium chloride produces trisodium phosphate.[394] With all of these reactions, except that with concentrated sulphuric acid, difficulty is experienced in separating the iron compounds from the phosphorus compounds and they cannot therefore be considered to have any economic possibilities.

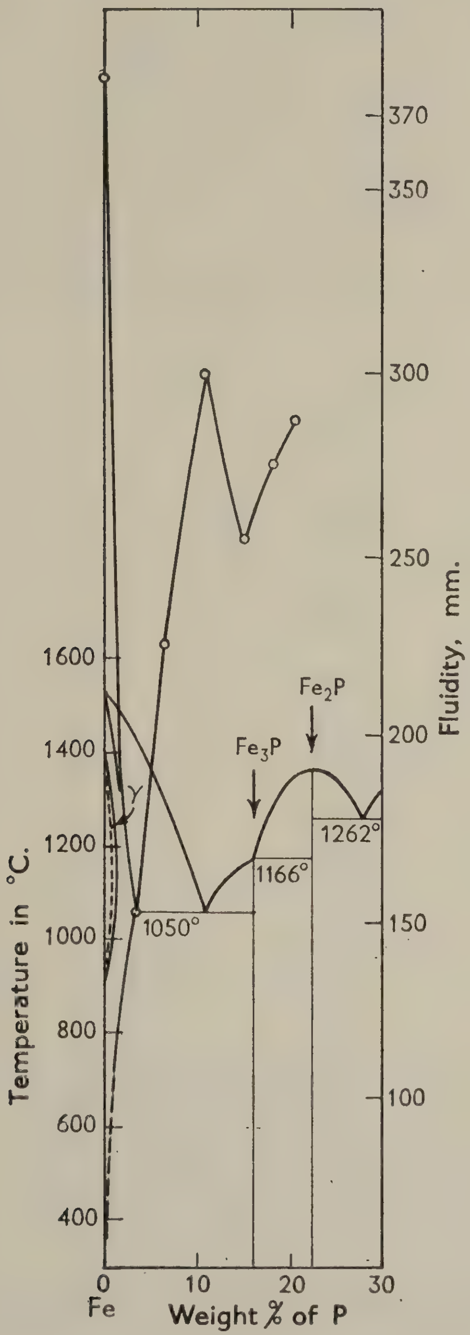

FIG. 25.—Structural and composition–fluidity diagrams for the iron–phosphorus system

Ferrophosphorus as such has been suggested as a heavy aggregate for dense concrete used in nuclear reactor shielding[395–403] and as an addition to green clay used in making refractory bricks. It is claimed that such addition eliminates the oxidation stage in the firing process (28 hr. at 500° to 980°C.).[404] A mixture of iron–phosphorus alloy and carbon is capable of reducing metal oxides to give pure metal or alloy[405] and a patent describes methods of obtaining alkali metals from a reaction between alkali metal carbonates and ferrophosphorus.[406] Phosphide-containing alloys have found some limited use because of their corrosion resistance,[407–9] and as brazing materials.[410] Physicochemical studies of the iron–phosphorus system have been made. Fluidities of molten alloys correlate well with the phase diagram shown in Fig. 25.[411–3] Experiments on undercooled alloys[414] show that phase differences exist between solid alloys formed from normal melts and those formed from undercooled melts. In these experiments it was found possible to establish the unstable iron–di-iron phosphide system.

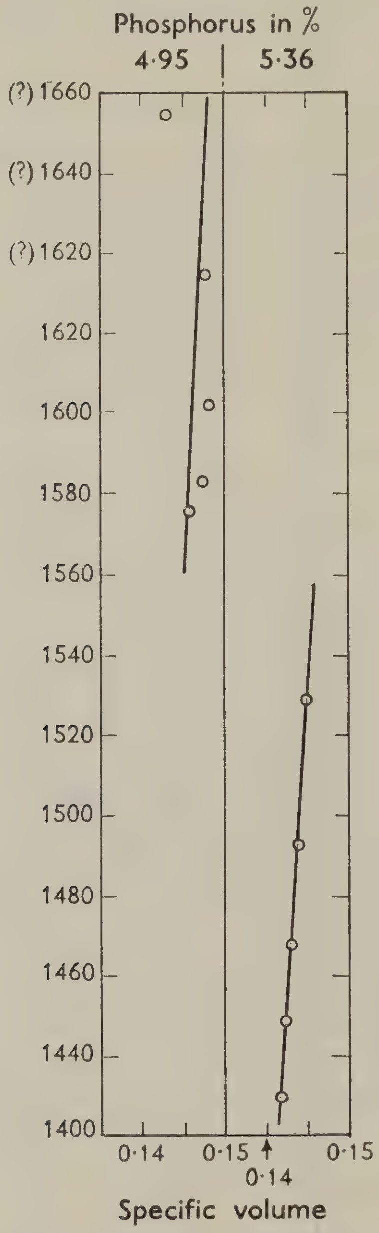

Fig. 26.—Specific volume of various iron alloys

In an effort to produce nickel-free alloys of high magnetic stability, the magnetic properties of iron–phosphorus alloys have been studied as a function of concentration and in relation to the precipitation phenomena.[415] Magnetostriction measurements show that the system is similar to the iron–tungsten system.[416] Alloys containing more than 1·5% of phosphorus are capable of precipitation hardening.[417] Hardness in annealed alloys shows an increase at 450°C., reaching a maximum at 550° to 600°C. Similarly electrical conductivity, coercivity and remanence show an increase and reach a maximum at 700° to 725°C.[417] Electromotive force measurements have been made on liquid alloys using the concentration cell:

$$\text{Fe, C}_{\text{satd.}}\text{, P} \mid \text{CaO, MgO, SiO}_2\text{, Ca}_3\text{P}_2\text{, Mg}_3\text{P}_2 \mid \text{Fe, C}_{\text{satd.}}\ \text{P}_{24\%}$$

With variation in phosphorus concentration of one electrode it was possible to show an inflexion at 22% of phosphorus and 1470°C. The composition corresponds to di-iron phosphide and the activity of the phosphorus indicated only slight dissociation for the compound.[418–9] Di-iron phosphide has also been noted as an inflexion at 22%P on magnetic susceptibility versus %P plots for the iron–phosphorus system.[420] Other magnetic susceptibility measurements have been made on dilute alloys (1·23 at.-% of phosphorus) but at temperatures around 1400°C.[421]

By studying the solubility of carbon in iron–phosphorus alloys at various temperatures, it was shown that phosphorus lowers the solubility of carbon in iron.[422] Activity coefficients of phosphorus[423] and specific volumes have also been measured.[424] The specific volumes of molten alloys are approximately proportional to the composition as shown in Fig. 26. Reaction diffusion was studied in the iron–phosphorus system: at 400° to 600°C. a unilateral diffusion of phosphorus was observed.[425]

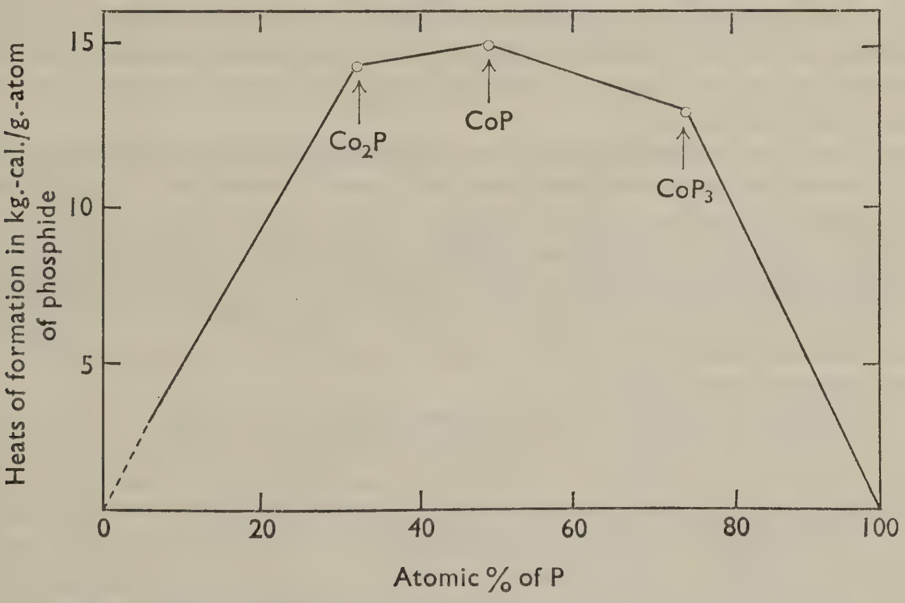

FIG. 27.—Heats of formation in the cobalt–phosphorus system

Investigations on ternary systems of iron and phosphorus with a third element are very numerous and in this class by far the most important, because of the relation to the iron and steel industries, are those dealing with the iron–phosphorus–carbon system.[426–41] In the iron–phosphorus–silicon system a new compound iron tetrasilicon tetraphosphide has been discovered.[442] Comparison of this system with analogous zirconium and titanium ones shows that the affinity for phosphorus is in the order $\text{Zr} > \text{Ti} > \text{Si}$.[442] The iron–phosphorus–niobium system was studied microscopically and by *X*-ray.[443] Three ternary compounds were found. FePNb melts congruently at 1820°C. and has *d* 4·99 g./c.c. $\text{FePNb}_2$ melts incongruently and so does $\text{FePNb}_4$. An investigation of the iron–phosphorus–boron system in the range $\text{Fe–FeP}_2\text{–BP–FeB–Fe}$ showed two ternary phases $\text{Fe}_5\text{PB}_2$ and $\text{Fe}_3\text{P}_{1-x}\text{B}_x$ which is homogeneous in the range $0{\cdot}48 < x < 1$ at 1000°C. $\text{Fe}_5\text{PB}_2$ is isostructural with $\text{Mn}_5\text{PB}_2$ and crystallizes with $a = 5{\cdot}482$, $c = 10{\cdot}332$ A., space group *I*4/*mcm*.[344]

Other investigations have been made of iron and phosphorus with silicon,[444–6, 442, 447] copper,[91, 94, 448] molybdenum,[449] nickel,[91, 450–2, 358] cobalt,[453–5] manganese,[91, 343, 455] chromium,[91, 310] tin,[455–6] vanadium,[455, 307–8] tungsten,[457] calcium,[116] beryllium,[100] aluminium,[458] sulphur,[459–60, 646–8] zinc,[167] oxygen[461] and titanium.[462] In this last mentioned system, thermal and structural investigations revealed a compound monoiron monotitanium monophosphide which has a congruent melting point of 1850°C. and a hardness of 980 kg./mm.$^2$ The iron–phosphorus–zirconium system is very similar to the iron–phosphorus–titanium system, and a compound monoiron monozirconium monophosphide having hardness 1150 kg./mm.$^2$ has been shown to exist.[463] Another compound, tetrairon monozirconium diphosphide, with hardness 1080 kg./mm.$^2$ has also been discovered, but no corresponding titanium compound has been reported.[463] Crystallographic data have been presented for the isostructural systems (Ti, Zr, Nb, Ta)FeP.[653]

Quaternary systems of iron and phosphorus with carbon and chromium,[430] carbon and manganese,[430] carbon and silicon,[440] silicon and oxygen,[464] carbon and molybdenum,[465] copper and platinum[466] have been studied, as well as the effect of phosphorus on the iron–manganese–silicon–oxygen system.[467]

### Cobalt

Tricobalt phosphide is thought to be one of the products when cobalt salts react with sodium hypophosphite, but the reaction tends to give intermetallic compounds rather than true phosphides.[468–9] In an examination of the Fe–$Fe_2P$–$Co_2P$–Co portion of the cobalt–phosphorus–iron system, tricobalt phosphide could not be established although there is a solid solution $(Co,Fe)_3P$.[453–4] Treatment with dilute hydrochloric acid of the products obtained from the above hypophosphite reaction converts them mainly to cobalt monophosphide, but a small amount of dicobalt triphosphide is formed as well.[468]

The reaction of a heated mixture of cobalt powder and red phosphorus has been used to produce dicobalt monophosphide for vapour pressure and *X*-ray studies.[470, 50] Andrieux's method, under the correct conditions of melt composition, voltage and current, also produces dicobalt phosphide.[10, 9, 311–2] The reduction of cobalt phosphates with hydrogen can also produce variable results. Dicobalt phosphide and monocobalt phosphide are produced if cobalt orthophosphate is reduced at 550°C., while a mixture of dicobalt phosphide and phosphorus is produced if cobalt metaphosphate is reduced at 675°C.[43]

Fig. 27 shows the heats of formation of some cobalt phosphides.[50] The free energy of formation of solid $Co_2P$ from the gaseous elements at $T$°K. is given by $\Delta G = -58{,}400 + 11{\cdot}3T$ g.-cal./mole.[548] *X*-Ray measurements have shown dicobalt phosphide to possess a crystal structure of the lead chloride type[471, 364] with $a = 6{\cdot}63(8)$–$6{\cdot}68(2)$ A., $b = 5{\cdot}67(0)$–$5{\cdot}75(1)$ A., $c = 3{\cdot}52(0)$–$3{\cdot}53(5)$ A.,[471] or $a = 5{\cdot}646$–$5{\cdot}638$ A., $b = 3{\cdot}513$–$3{\cdot}507$ A., $c = 6{\cdot}608$–$6{\cdot}603$ A.[472] The variations in lattice parameters are due to the fact that the compound has an extended homogeneity range, the P-rich limit at 1000°C. corresponding to $Co_{1{\cdot}94}P$.[471–2] The molecular volume from *X*-ray data is 10·3 c.c.[470]

If the compound is deposited electrolytically on flat surfaces or wires there is a preferred orientation and the crystals deposit with [001] axes perpendicular to the surface.[364] The results of vapour pressure measurements for this phosphide and others are summarized in Fig. 28.[470]

Dicobalt phosphide is attacked by oxidizing acids such as nitric acid and aqua regia.[470] Alloys with $Ni_2P$ are single phase,[311] while alloys with $Fe_2P$ are suitable for the manufacture of permanent magnets.[649]

Tricobalt diphosphide is formed as a finely divided, air sensitive precipitate when cobalt chloride in tetrahydrofuran reacts with $[(CH_3)_3Si]_3P$. The reaction goes according to equation 31[473]:

$$(31) \qquad 2[(CH_3)_3Si]_3P + 3CoCl_2 \rightarrow Co_3P_2 + 6Si(CH_3)_3Cl$$

Monocobalt phosphide has been obtained by the same methods as dicobalt phosphide. In the method using sodium hypophosphite it has not been obtained in a pure state.[468] Heating cobalt orthophosphate at 550°C. in an atmosphere of hydrogen gives a mixture of mono- and di-cobalt phosphides[43] but cobalt pyrophosphate is converted only into monocobalt phosphide.[43] The electrolysis of phosphate melts containing cobalt salts[10, 9, 311–2] and heating together red phosphorus and cobalt have also been used as methods of preparation. In this latter preparation, vapour pressure measurements, *X*-ray photographs, and thermal measurements confirmed the presence of monocobalt phosphide.[470–1] It has the MnP type of structure,[313, 322, 471] with $a=5{\cdot}077$, $b=3{\cdot}281$, $c=5{\cdot}587$ A.,[313] or $a=5{\cdot}588$, $b=5{\cdot}066$, $c=3{\cdot}274$ A.[322] It is

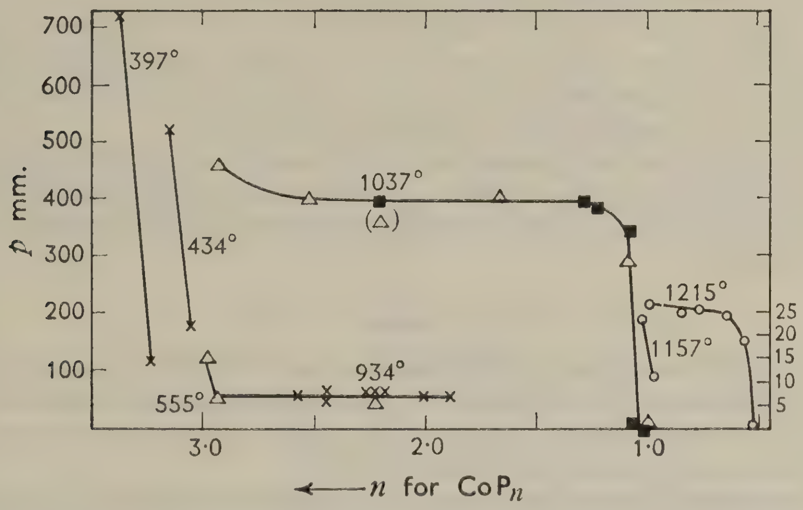

FIG. 28.—Vapour pressure analysis in the cobalt–phosphorus system

capable of forming solid solutions with FeP, MnP and CrP. Boron dissolves to some extent and silicon shows considerable solubility.[313] The heat of formation is shown in Fig. 27,[50] whilst equations (32) and (33) were established by means of v.p. measurements.

$$\text{(32)} \qquad \tfrac{1}{2}\mathrm{CoP(s)} + \mathrm{P(rhomb.)} \rightarrow \tfrac{1}{2}\mathrm{CoP_3(s)} \qquad \Delta H = -15 \text{ kcal.}$$

$$\text{(33)} \qquad 4\mathrm{CoP(s)} \rightarrow 2\mathrm{Co_2P(s)} + \mathrm{P_2(g)} \qquad \Delta H = +69 \text{ kcal.}$$

Assumptions were made concerning the temperature dependence of the dissociation of monocobalt phosphide.[470] The free energy of formation of solid CoP from the gaseous elements at $T$°K. is given by the expression $\Delta G = -49{,}400 + 11{\cdot}3T$ g.-cal./mole.[548] In an investigation into the use of monocobalt phosphide in corrosion resistant anodes its rates of corrosion in hydrochloric acid, sulphuric acid, nitric acid and potassium hydroxide were determined at 25°C. and 80°C.[365] Current–voltage curves were also plotted for various liquids.[365] Monocobalt phosphide is attacked by nitric acid and aqua regia[470] and it is oxidized to cobaltous and orthophosphate ions when used as anode material in acid, alkaline or acetate solutions.[365]

Andrieux's method of electrolyzing alkaline phosphate melts has been shown to produce cobalt diphosphide.[10, 9]

A rather unusual reaction between cobalthexammine nitrate and monopotassium phosphine in liquid ammonia gives a dark brown pyrophoric powder, $\mathrm{Co(PH_2)_3}$, which decomposes spontaneously to give $\mathrm{Co(PH)_3}$. If this is then heated to 560°C. a crystalline substance with the composition $\mathrm{CoP_{2{\cdot}37}}$ is formed.[474]

Cobalt triphosphide, required for an *X*-ray, vapour pressure, and thermal study,[470] was prepared by reaction of the elements. From the *X*-ray measurements a molecular volume of 35·7 c.c. was calculated. The v.p. measurements (which are shown in Fig. 28) were used to establish equation (34):

$$\text{(34)} \quad 2\mathrm{CoP_3(s)} \rightarrow 2\mathrm{CoP(s)} + \mathrm{P_4(g)} \qquad \Delta H = +72 \text{ kcal.} \qquad t \sim 900\text{–}1050°\text{C.}$$

The free energy of formation of solid $\mathrm{CoP_3}$ from the gaseous elements at $T$°K. is calculated to be $\Delta G = -103{,}200 + 33{\cdot}8T$ g.-cal./mole.[548]

Electrodeposition of cobalt containing up to 15% of phosphorus has been achieved from acid solutions, but it was not possible to establish the existence of a phosphide.[475] In the cobalt–phosphorus system, the effect of phosphorus on the $\alpha \rightleftharpoons \beta$ transformation of cobalt has been studied[476] and the mechanism of reaction-type diffusion was investigated.[425] At 400° to 600°C. a unilateral diffusion of phosphorus was observed.[425] Cobalt phosphides have been used for protecting alloys prone to air oxidation[316] and for joining metals with high melting points.[477]

In the ternary system cobalt–phosphorus–boron, three ternary phases were found[344]: $Co_3P_{1-x}B_x$ is homogeneous in a narrow range near $x=0{\cdot}7$, $Co_3P_{1-y}B_y$ is homogeneous in a range near $y=0{\cdot}5$ and is isostructural with $Fe_3P$ and finally $Co_5PB_2$ which is isostructural with $Fe_5PB_2$ and $Mn_5PB_2$.

A semiconducting ternary compound CoPS has been described having a cubic cobaltite (CoAsS) lattice with $a=5{\cdot}422$ A.[569] A ternary compound $CoPS_3$ has been described.[648] Crystallographic data have been presented for the isostructural phases (Ti, Zr, Nb, Ta)CoP.[653]

## Nickel

Although not all the nickel phosphides reported in the literature have been confirmed, it is still probably true to say that nickel forms more phosphides than any other element with the possible exception of cobalt. A tentative phase diagram has been presented which includes ten binary phases.[651]

Trinickel phosphide is the lowest one which has been reported. Several methods have been used for its preparation and of these two are the familiar Andrieux's method[10, 9, 311–2] and reaction of the elements in a sealed tube.[50] The reaction of sodium dihydrogen hypophosphite with nickel sulphate solution gives compositions in the range $Ni_{3{\cdot}18}P$ to $Ni_{3{\cdot}48}P$. These preparations are not homogeneous, however, and contain nickel metal.[478] Nickel–tin alloys heated with red phosphorus at 550° to 700°C. for 5 to 56 hr. produce a mixture of phosphides one of which has been shown to be trinickel phosphide by *X*-ray, thermal, and tensimetric analysis.[479] *X*-Ray studies have also identified this phosphide in heat treated chemically deposited nickel coatings containing 7 to 10·5% of phosphorus,[480] and in precipitates of chemically reduced nickel.[481–2] The crystal structure of trinickel phosphide is tetragonal with space group $I\bar{4}$ and unit cell dimensions $a=8{\cdot}923$, $c=4{\cdot}40$ A.[481]; $a=8{\cdot}954$, $c=4{\cdot}386$ A.[483–4]; $a=8{\cdot}91(6)$, $c=4{\cdot}38(9)$ A.[485] Density 7·9 g./c.c. was determined from *X*-ray measurements.[485] The heat of formation from the elements is −48·4 kcal./mole and is shown in Fig. 29, together with heats of formation of other nickel phos-

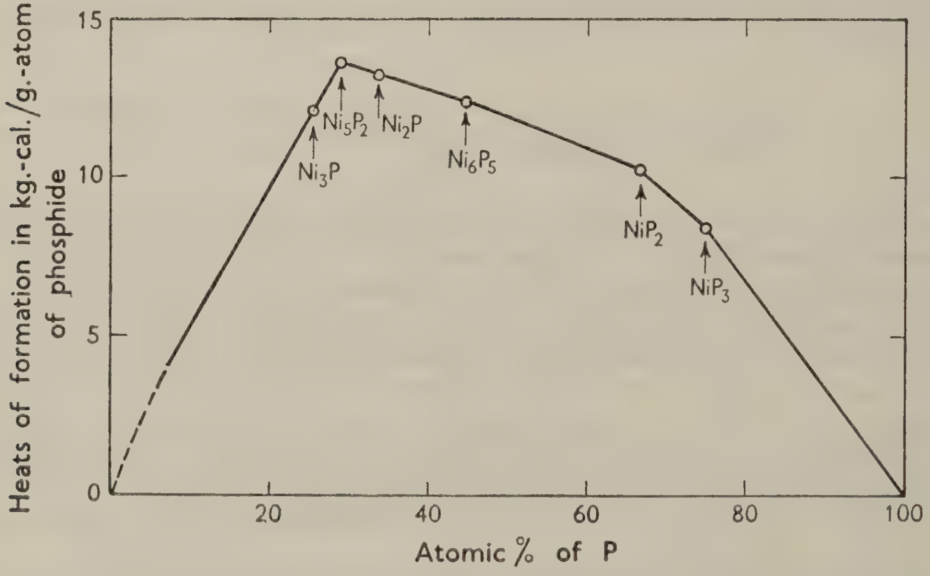

FIG. 29.—Heats of formation of nickel phosphides

phides.[50] Trinickel phosphide is insoluble in hot concentrated hydrochloric acid but is easily soluble in warm nitric acid.[479] It has been shown to be isomorphous with the corresponding iron and manganese compounds[485, 91] but forms a continuous series of mixed crystals only with tri-iron phosphide. Trichromium phosphide is only slightly miscible although 50% of the non-isotype tricopper phosphide can be dissolved.[91] An alloy consisting of trinickel phosphide and nickel, produced from spent nickel plating baths, has been used for bonding metal surfaces and for flame spraying on to various surfaces.[486–7]

Pentanickel diphosphide has been produced by reaction of the elements[50] and by Andrieux's method.[10, 9] Under carefully controlled conditions it can be obtained by the action of phosphine on nickel salt solutions.[488] In ammonia solution, for example, trinickel diphosphide is produced, some of which reacts with excess of nickel salt to give nickel and this in turn reacts with more trinickel diphosphide to give pentanickel diphosphide.[488] The reactions involved may proceed according to equations (35), (36), (37) and (38):

$$3NiX_2+2PH_3 \rightarrow Ni_3P_2+6HX \tag{35}$$

$$Ni_3P_2+5NiX_2+8H_2O \rightarrow 8Ni+2H_3PO_4+10HX \tag{36}$$

$$Ni_3P_2+3NiX_2+6H_2O \rightarrow 6Ni+2H_3PO_3+6HX \tag{37}$$

$$Ni_3P_2+2Ni \rightarrow Ni_5P_2 \tag{38}$$

The action of sodium hypophosphite on various nickel salts has been investigated and although the products were not considered as being true phosphides, material corresponding to pentanickel diphosphide has been obtained by reaction with acetic acid.[489, 468] The structure of pentanickel diphosphide is in debate, the compound having either an hexagonal lattice with $a=13{\cdot}220$, $c=24{\cdot}632$ A.[650] or a trigonal cell with $a=6{\cdot}608$, $c=24{\cdot}634$ A.[651] A high temperature $\beta$-form of $Ni_5P_2$ is obtained by quenching $Ni_{2\cdot60}P$ from 1050°.[651] This phosphide is a black non-magnetic compound[488] with a heat of formation from the elements of $-95{\cdot}9$ kcal./mole[50] (see Fig. 29), and a free energy of formation (from the gaseous elements at $T$°K.) given by $\Delta G=-126{,}300+22{\cdot}5T$ g.-cal./mole.[548] It is homogeneous at 28·2 at.-% P, but a composition with the theoretical 28·6 at.-% P contains some $Ni_{12}P_5$.[651] It can be converted into dinickel phosphide by ignition in hydrogen at 800°C.[488] or by treatment with hydrochloric acid.[489] Dilute hydrochloric acid reacts to give nickel chloride according to equation (39)[488–9]:

$$Ni_5P_2+10HCl+6H_2O \rightarrow 5NiCl_2+2H_3PO_3+8H_2 \tag{39}$$

In an investigation of the nickel–phosphorus system it was shown that crystallization of undercooled alloys could produce an unstable system nickel–pentanickel diphosphide.[414]

In an *X*-ray study of the nickel–phosphorus system a compound heptanickel triphosphide was shown to be cubic with $a=8{\cdot}63(0)$ A.[485] Additional weak lines indicated possible lower symmetry and, if the compound $Ni_{2\cdot4}P$ reported in a later *X*-ray investigation is the same compound, then the crystal system is not cubic but tetragonal with cell dimensions $a=8{\cdot}646$, $c=5{\cdot}070$ A.[484] and the compound should be $Ni_{12}P_5$ and not $Ni_7P_3$.[651] It has been prepared by Andrieux's method.[311–2]

Reduction of nickel phosphates with hydrogen at 450° to 600°C. and with continual removal of the water vapour formed produces dinickel phosphide[43] as does Andrieux's method[10, 9, 311–2] or heating a tin–nickel alloy with red phosphorus.[479] In the action of an alkali metal hypophosphite on a nickel salt, intermetallic compounds are produced which yield a product $Ni_2P$ or $Ni_4P_2$ when treated with dilute hydrochloric acid.[489, 478] *X*-Ray measurements indicate that dinickel phosphide is hexagonal with $a=5{\cdot}85(0)$, $c=3{\cdot}365$ A.[485] or $a=5{\cdot}859$, $c=3{\cdot}382$ A.[484, 320]; $d$ 7·2 g./c.c.[485] Electrodeposition experiments show that dinickel phosphide orients itself with its [1120] axis parallel to the surface upon which it is being deposited.[364] It is isomorphous with di-iron phosphide and dimanganese phosphide[485] and forms a series of mixed crystals with these, as well as with dichromium phosphide.[91] Like dimanganese phosphide, it exhibits an appreciable homogeneity range.[320] The reaction in equation (40):

$$(40)\qquad \tfrac{3}{2}Ni_2P(s) + P(white) \rightarrow \tfrac{1}{2}Ni_6P_5(s) \qquad \Delta H = -12 \text{ kcal.}$$

has been established from tensimetric measurements.[479] The free energy of formation of solid dinickel phosphide from the gaseous elements at $T$°K. is said to follow the expression $\Delta G = -55{,}400 + 11{\cdot}3T$ g.-cal./mole over the range 298–1383°K.[548] There is no reaction with hot concentrated hydrochloric acid,[479] but it reacts easily with dilute hydrochloric acid according to equation (41).[489]

$$(41)\qquad Ni_2P + 4HCl + 3H_2O \rightarrow 2NiCl_2 + H_3PO_3 + \tfrac{7}{2}H_2$$

Dinickel phosphide has been studied as a catalyst for the conversion of nitrobenzene into aniline[490] and for the polymerization of $\alpha$-olefins.[491]

It has been reported that a trinickel diphosphide can be obtained by reaction of phosphine with ammoniacal nickel salt solutions. It is easily decomposed by water and dilute acids.[488] Alloys in the range $Ni_2P$–$Ni_{1\cdot25}P$ quenched from temperatures below 850° give a mixture of dinickel phosphide and pentanickel tetraphosphide (hexagonal, $a = 6{\cdot}789$, $c = 10{\cdot}986$ A.). Above this temperature $Ni_2P$ and NiP are the stable phases.[651–2]

Andrieux's method,[10, 9] or heating a nickel–tin alloy with red phosphorus at 550° to 700°C.,[479] produces hexanickel pentaphosphide. It has been identified by $X$-ray, thermal, and tensimetric means. Its heat of formation is shown in Fig. 29 and from vapour pressure measurements equations (42), (43) and (44) were established[479]

$$(42)\qquad 2Ni_6P_5(s) \rightarrow 6Ni_2P(s) + P_4(g) \qquad \Delta H = +63 \text{ kcal.}$$

$$(43)\qquad \tfrac{1}{7}Ni_6P_5(s) + P(white) \rightarrow \tfrac{6}{7}NiP_2 \qquad \Delta H = -11 \text{ kcal.}$$

$$(44)\qquad \log p_{(mm.)} = -13{,}740/T + 14{\cdot}951$$

A reaction which appears to have been tried only in the case of nickel phosphides is that of nickel tetracarbonyl with phosphorus or phosphine at 50°C.[492] Mononickel phosphide is deposited as black, non-magnetic crystals which are converted into nickel orthophosphate when heated in air.[492] The lattice is orthorhombic with $a = 6{\cdot}050$, $b = 4{\cdot}881$, $c = 6{\cdot}890$ A.[651] It is scarcely attacked by dilute hydrochloric acid, but is easily soluble in nitric acid and aqua regia.[492] The free energy of formation of solid mononickel phosphide from the gaseous elements at $T$°K. is given by the expression $\Delta G = -63{,}800 + 11{\cdot}3T$ g.-cal./mole over the range 298–1243°K.[548]

The reaction of red phosphorus with a nickel–tin alloy at 550° to 700°C. produces several phosphides, one of which is nickel diphosphide.[479] It has also been synthesized by heating mixtures of metal powder and red phosphorus in evacuated sealed silica tubes at 800° to 1100°C.[493] $X$-Ray investigations have shown it to be monoclinic with $a = 6{\cdot}365(9)$, $b = 5{\cdot}615(2)$, $c = 6{\cdot}071(5)$ A., $\beta = 126{\cdot}22(4)°$ and space group probably $C2/c$ or $Cc$.[493, 651] Vapour pressure measurements enabled investigators to establish equations (45) and (46)[479]:

$$(45)\qquad \tfrac{24}{7}NiP_2(s) \rightarrow \tfrac{4}{7}Ni_6P_5(s) + P_4(g) \qquad \Delta H = +57 \text{ kcal.}$$

$$(46)\qquad \log p_{(mm.)} = -12430/T + 14{\cdot}135$$

The free energy of formation of solid nickel diphosphide from the gaseous elements at $T$°K. is $\Delta G = -62{,}800 + 22{\cdot}5T$ g.-cal./mole.[548]

The reaction discussed for nickel diphosphide was also shown to produce nickel triphosphide. $X$-Ray, thermal and tensimetric analyses were used to prove its existence.[479] The variation of vapour pressure with temperature obeys equation (47):

$$(47)\qquad \log p_{(mm.)} = -9340/T + 12{\cdot}865$$

and thermochemical calculations using the vapour pressure data enabled equation (48) to be established[479]:

$$(48)\qquad 4NiP_3(s) \rightarrow 4NiP_2(s) + P_4(g) \qquad \Delta H = +43 \text{ kcal.}$$

The heat of formation is shown in Fig. 29, and the free energy of formation of the solid phosphide from the gaseous elements at $T$°K. is given by $\Delta G = -82{,}200+33{\cdot}8T$ g.-cal./mole.[548] Electrical properties of the compound have been reported.[660] Nickel triphosphide is soluble in warm nitric acid but not in hot concentrated hydrochloric acid.[479]

By bubbling nickel tetracarbonyl through liquid phosphorus at 60°C. or through a solution of phosphorus in turpentine, a black precipitate was obtained which was thought to be nickel tetraphosphide.[492] It is a rather unstable powder and evolves phosphorus when heated in air. Fuming nitric acid makes it inflame whilst aqueous potassium hydroxide and aqueous ammonia produce phosphine and hydrogen.[492]

An electrically conducting ternary sulphide, NiPS, having a cubic cobaltite (CoAsS) lattice with $a=5{\cdot}544$ A., has been reported.[569]

Electrodeposition of nickel–phosphorus alloys from solutions containing $Ni^{++}$ and $PO_4^{3-}$ ions has been attributed to direct absorption of phosphorus from the electrolyte at the electrode.[494] Partial investigations in the ternary systems nickel–phosphorus–iron,[451, 91, 450, 452, 358] nickel–phosphorus–chromium,[91, 308] nickel–phosphorus–manganese,[91] nickel–phosphorus–copper[91–2] and nickel–phosphorus–boron[344] have been made. In the nickel–phosphorus–iron system $X$-ray methods established the presence of $Ni_2P$, $Ni_3P$, $Ni_7P$, $(Fe, Ni)_2P$,$(Fe, Ni)_3P$ and a compound containing more nickel than $Ni_3P$.[358] Defects in German-silver alloys have been traced to the formation of nickel phosphides.[495]

Few uses of nickel phosphides have been noted, the main ones being as catalysts,[73, 490] for bonding metal surfaces,[477, 486–7] as a protection for metal surfaces[496, 316] and as components of friction elements such as brake linings.[75]

## THE SECOND TRANSITION SERIES

### Yttrium

Yttrium monophosphide has been prepared by heating the powdered metal with red phosphorus in a silica tube at 1000° for 30 hr. It forms cubic crystals in the NaCl system, $a=5{\cdot}661$ A.,[564] 5·662 A.[547, 654]

### Zirconium

A phosphide, possibly trizirconium phosphide, has been claimed to be formed by heating powdered metal and red phosphorus in a pressure tube for 7 hr. at 500° to 600°C. followed by 24 hr. at 800°C. and finally 8 days at 900° to 1000°C.[497] If the reaction tube is cooled slowly, at approximately 100°C. per hour, a grey product is obtained. Existence of a phosphide within the range $ZrP_{0{\cdot}3-0{\cdot}5}$ was confirmed by $X$-ray analysis of material obtained by heating zirconium diphosphide with metal powder.[292]

Two methods of preparing zirconium monophosphide both start from the diphosphide. In one case the diphosphide is heated in a vacuum at 750°C. when phosphorus is readily evolved[497] and in the other case it is heated with powdered zirconium. As with some other transition-metal phosphides, zirconium monophosphide has been shown to exist in two forms.[292] The $\beta$-form has the stoicheiometric composition ZrP. It is a grey-black compound which does not oxidize or decompose in air below 1100°C.[497] It has a density of 5·35 g./c.c.[292] It forms hexagonal crystals isomorphous with titanium monophosphide,[292, 570] having the cell dimensions $a=3{\cdot}684$, $c=12{\cdot}554$ A. On heating this compound, these values increase almost linearly with temperature, until at 1425°C. *in vacuo* the system transforms smoothly to the deficient $\alpha$ form, $ZrP_{0{\cdot}9}$, with evolution of phosphorus. The partial molal enthalpy of dissociation of $ZrP_{0{\cdot}92}$ to $P_2$ is 66·8 kcal./mole $P_2$ at 1500°K. and 51·1 kcal./mole at 2000°K.[631] $\alpha$-ZrP forms face centred cubic crystals, $a=5{\cdot}242$ A., stable *in vacuo* above 1425°C.[570] and having a density of 5·1 g./c.c.[292]

Zirconium diphosphide is readily prepared by heating powdered zirconium with red phosphorus in an evacuated sealed vessel[296, 497, 292] or by heating powdered zirconium in a mixture of phosphine and hydrogen.[292] The first method has been patented as a means of manufacture.[306] Zirconium diphosphide has an orthorhombic lattice, with $a=6{\cdot}494$, $b=8{\cdot}744$, $c=3{\cdot}513$ A.[637] Results of v.p. measurements shown in Fig. 30[497] were used to calculate the heat of decomposition according to equation (49):

$$(49) \qquad 4ZrP_2(s) \rightarrow 4ZrP(s) + P_4(g) \qquad \Delta H = +50 \text{ kcal.}$$

The compound is attacked slowly by dilute sulphuric acid to evolve phosphine but is stable in the atmosphere and is not attacked appreciably even by mixtures of bromine with nitric acid.[497]

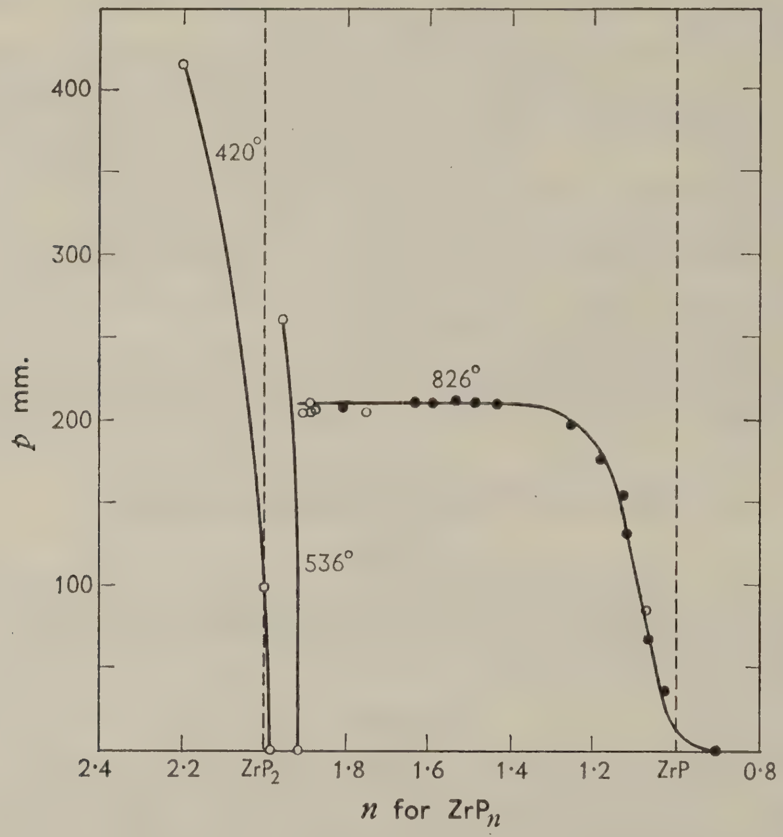

FIG. 30.—Vapour pressure analysis of $ZrP_2$ and ZrP

The ternary systems Zr–Fe–P and Zr–Co–P have been investigated structurally. ZrFeP has space group *Pnma* with $a=6{\cdot}309$, $b=3{\cdot}740$, $c=7{\cdot}172$ A. and ZrCoP has $a=6{\cdot}332$, $b=3{\cdot}698$, $c=7{\cdot}160$ A.[653]

### Niobium [Columbium]

Triniobium phosphide, which has a structure of the $Ti_3P$ type, has been obtained by rapidly annealing in an argon arc furnace an alloy prepared from red phosphorus and niobium in an evacuated silica tube.[655] Heptaniobium tetraphosphide (monoclinic, $a=14{\cdot}950$, $b=3{\cdot}440$, $c=13{\cdot}848$ A., $\beta=104{\cdot}74$) has been made similarly.[686]

Niobium monophosphide is prepared by heating the metal with red phosphorus at 650° to 850°C. for several days[498–9] or with tricalcium diphosphide,[566] or by electrolyzing phosphate melts containing niobium oxide.[304] An *X*-ray investigation has shown that there are two modifications,[292] thus supporting previous work.[498] The $\alpha$ variety is approximately $NbP_{0{\cdot}95}$ and the $\beta$ form is NbP. The $\beta$ form has $d$ 6·15 g./c.c.[292] (5·91 g./c.c.[499]) and molecular volume 21·1 c.c.[499] and it was suggested that the structure was a distorted nickel arsenide type.[305] Later authors, while confirming the tetragonal cell dimensions $a=3{\cdot}33$, $c=11{\cdot}37$ A., have shown that $\beta$-NbP is isomorphous with niobium arsenide.[563, 655] They suggest that the distinction between α-NbP and β-NbP is meaningless since 'α-NbP' compositions are members of a continuous series of structures, in which the NbAs lattice of β-NbP is disordered more and more towards a tungsten carbide lattice as the phosphorus becomes more deficient.[563] The partial molal enthalpy of dissociation to $P_2$ of $NbP_{0{\cdot}95}$ is 55·4 (1000°K.) and 34·0 (1500°K.) kcal./mole $P_2$.[631] The two forms are isomorphous with the corresponding α and β tantalum phosphides.[292, 305, 498] Both forms are greyish black materials having a metallic lustre.[292, 499] They are not attacked by water or dilute acids at room temperature but a brisk reaction takes place with concentrated nitric acid.[499] Heating in air produces a white oxide the nature of which has not been determined.[499] In an inert atmosphere the phosphide is stable up to 1750°C.[566]

Niobium diphosphide could not be prepared by heating the metal with red phosphorus.[498] It was prepared, however, by removing phosphorus from a composition $NbP_{2{\cdot}4}$ under vacuum at 430°C.[498] and by heating the metal powder in a mixture of phosphine and hydrogen.[292] It is isomorphous with the tantalum and vanadium phosphides,[498, 292] having $a=8{\cdot}8715$, $b=3{\cdot}2663$, $c=7{\cdot}5194$ A., $\beta=119{\cdot}007°$,[655] with which it has been compared.[305] As with vanadium diphosphide, it is not attacked by dilute sulphuric acid but is completely dissolved by the concentrated acid.[301] It also has properties similar to molybdenum and tungsten diphosphides since it is not dissolved by concentrated hydrochloric acid or ammoniacal hydrogen peroxide.[499] Above 650°C. it disproportionates to give niobium monophosphide and phosphorus.[498]

Several methods which have been used to study a portion of the Nb–P–Fe system have resulted in the recognition of three ternary compounds. Niobium iron phosphide melts congruently at 1820°C. and has *d* 4·99 g./c.c. whilst diniobium iron phosphide and tetraniobium iron phosphide both melt incongruently. The hardness of these compounds is 1322, 1238 and 1063 H.V., respectively.[443] Unit cell constants have been determined for NbFeP and NbCoP.[653]

## Molybdenum

Trimolybdenum phosphide can be prepared by electrolyzing fused alkali metal phosphates containing molybdenum compounds[10, 500–1, 9, 311–2] or by heating the elements together in a sealed quartz tube.[315] The compound crystallizes as fine black needles having a metallic lustre.[500] Although the crystal lattice is body-centred tetragonal it seems that it may be isostructural with $\alpha\text{-}V_3S$[571] rather than tri-iron phosphide.[315, 292] The space group is $I\bar{4}2m$, and the lattice parameters $a=9{\cdot}794$, $c=4{\cdot}827$ A.[656] Its density has been variously reported as 6·7 g./c.c.[500] and 8·6 g./c.c.[292] The latter value would fit better a straight line plot of density against composition as shown in Fig. 31. Trimolybdenum phosphide becomes superconducting at 7°K.[53, 502] It is attacked by sulphuric acid, nitric acid, molten alkali or oxidizing agents[500] but not by hydrochloric acid.

Besides the three well-established phosphides of molybdenum, a deficient phase of approximate composition $MoP_{0{\cdot}75}$ is said to occur.[571] It crystallizes in space group *Pnma* with $a=12{\cdot}428$, $b=3{\cdot}158$, $c=20{\cdot}440$ A.[657]

Monomolybdenum phosphide is formed in the above electrolytic method when the molybdenum-compound content of the melt is low (approximately 4%).[9–10, 500–1, 311–2] It has also been made by causing the metal to react with tricalcium diphosphide.[566] *X*-Ray and tensimetric analysis confirmed its formation from the elements.[315] The results of the tensimetric analysis are shown in Fig. 32. Monomolybdenum phosphide is a greyish black compound[500] which has *d* 7·2 g./c.c., the tungsten carbide type of structure[292, 571] and no superconductivity.[502, 53] Its average molal enthalpy of decomposition ($\Delta H_{1360°\text{K.}}$) is 107·84 kcal./mole $P_2$. The decomposition products at 1250°C. are phosphorus and an involatile phase $MoP_{0{\cdot}7}$, which is predicted as being unstable below 700° to give the monophosphide and a phosphide of lower phosphorus content.[658] It reacts readily with nitric acid, molten alkali, and oxidizing agents.[500]

The diphosphide is obtained easily by heating a slight excess of red phosphorus with powdered molybdenum at 550°C. for 24 hr.[499] and by passing a mixture of phosphine and hydrogen over the heated metal.[292] It is a black powder having *d* 5·3 g./c.c.,[499] and crystallizing in the orthorhombic system.[571] The heat of dissociation, from tensimetric measurements shown in Fig. 32, is 10 kcal./mole.[315] When the phosphide is free from phosphorus it is stable in dry air. Oxidizing acids attack it but it is stable in concentrated hydrochloric acid and ammoniacal hydrogen peroxide.[499]

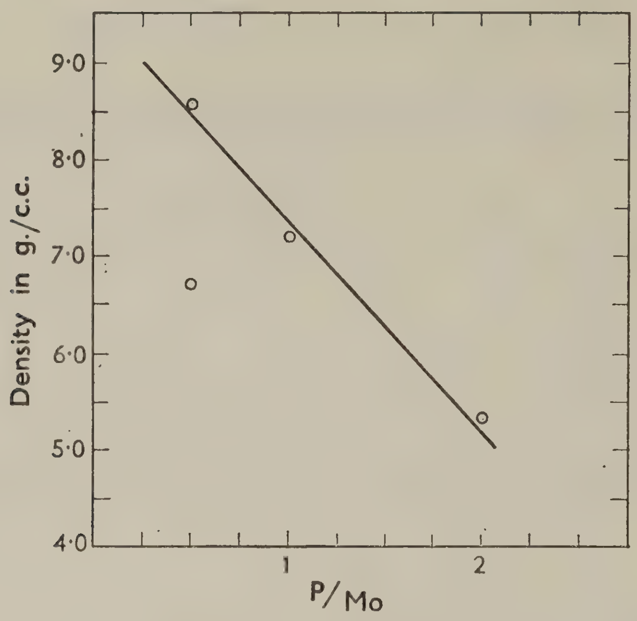

FIG. 31.—Plot of density of molybdenum phosphides against their phosphorus to molybdenum ratio

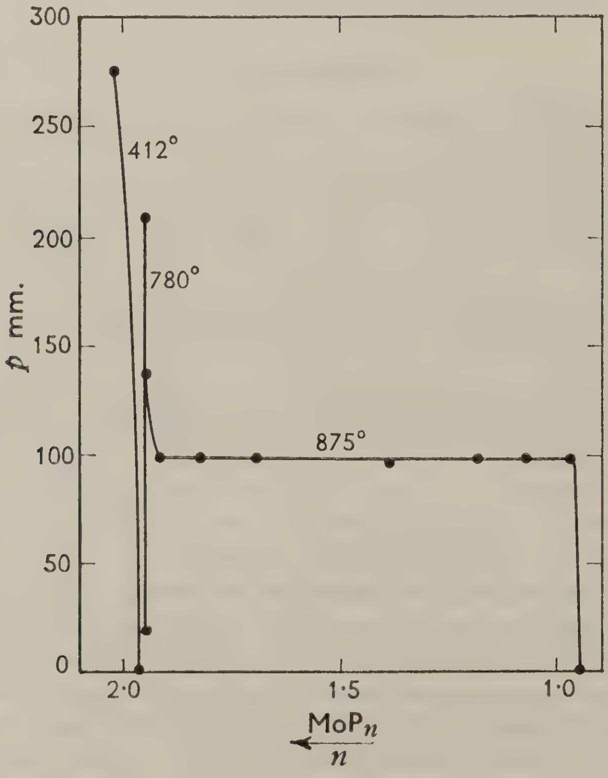

FIG. 32.—Vapour pressure analysis for molybdenum phosphides

A partial investigation of the molybdenum–phosphorus–iron system has been made.[449]

## Ruthenium

Diruthenium phosphide can be prepared by reaction of ruthenium with red phosphorus[472, 503] or by heating ruthenium diphosphide *in vacuo* at a high temperature.[503] It crystallizes with an anti-lead chloride type of structure, space group *Pnma* and unit cell dimensions $a = 5{\cdot}902$, $b = 3{\cdot}859$, $c = 6{\cdot}896$ A.[504, 472] This phosphide, like ruthenium monophosphide but unlike dirhodium phosphide, does not become superconductive at low temperatures.[572] It is very resistant to attack by alkaline solutions and is hardly attacked by aqua regia.[503]

Ruthenium monophosphide has also been obtained by direct reaction of the elements at elevated temperatures.[503, 313] The reverse reaction of formation of ruthenium diphosphide from ruthenium monophosphide and phosphorus proceeds according to equation (50)[503]:

$$(50)\quad 2RuP(s) + P_2(g) \rightarrow 2RuP_2(s) \qquad \Delta H = -65 \text{ kcal.} \qquad t = 650\text{–}680°C.$$

It crystallizes with a manganese monophosphide type of structure, space group *Pnma* and unit cell dimensions $a = 5{\cdot}520$, $b = 3{\cdot}168$, $c = 6{\cdot}120$ A.[313, 504] The compound is blue-black, similar to diruthenium phosphide but not quite as resistant to aqua regia.[503]

Ruthenium diphosphide has been prepared by the same method as the above two phosphides. It is a black compound which has the marcasite type of structure[504, 645] and is resistant to attack by alkaline solutions.[503] It is a semiconductor, having an energy gap of ~1 e.v., a Seebeck coefficient of approximately $350\mu V/°C.$ and a magnetic susceptibility, $\chi_{\text{mol}}$, of $-44 \times 10^{-6}$ c.g.s. units at 295°K.[573]

Similar data have been recorded for the semiconductive compounds RuPS and RuPSe. They have a monoclinic arsenopyrite structure with $a = 5{\cdot}77$, $b = 5{\cdot}77$, $c = 5{\cdot}81$ A., $\beta = 111{\cdot}2°$ (RuPS) and $a = 5{\cdot}97$, $b = 5{\cdot}92$, $c = 5{\cdot}98$ A., $\beta = 111{\cdot}8°$ (RuPSe).[659]

The semiconductive ternary compound RuPAs has been described. It also has the marcasite type of structure, an energy gap of ~0·8 e.v., a Seebeck coefficient of $\sim 400\mu V/°C.$ and a magnetic susceptibility, $\chi_{\text{mol}}$, of $-61 \times 10^{-6}$ c.g.s. units at 295°K.[573]

## Rhodium

All of the known phosphides of rhodium have been prepared by heating rhodium with red phosphorus in a pressure tube at elevated temperatures.[505–6, 493] Dirhodium phosphide, pentarhodium tetraphosphide, rhodium diphosphide and rhodium triphosphide were all identified by *X*-ray and tensimetric analysis; the v.p. measurements are shown in Fig. 33.

Structural investigations have shown that dirhodium phosphide has a structure similar to that of diiridium phosphide which is of the fluorite type: $a = 5{\cdot}505$,[507] 5·490,[508] 5·498,[506] 5·516 A.[572] Its density is 9·13 g./c.c.,[505] the molecular volume is 26 c.c.[507, 505] and the m.p. is above 1500°C. The compound, which is grey, does not show superconductivity,[502] though this statement has been more recently denied.[572] Reaction with hot concentrated nitric acid and aqua regia is slight but with boiling sulphuric acid it is vigorous.[505]

Pentarhodium tetraphosphide reported above[505] has more recently been shown to be tetrarhodium triphosphide and its crystal structure has been determined. The space group is *Pnma* and unit cell dimensions are $a = 11{\cdot}662$, $b = 3{\cdot}317$, $c = 9{\cdot}994$ A. Its structure is related to that of $Fe_2P$ and resembles that of $Ni_4B_3$.[508, 506] Material reported as pentarhodium tetraphosphide, which was said to become superconducting at 1·22°K.,[502] has since been identified with dirhodium phosphide ($T_c$ 1·3°K.).[572]

Rhodium diphosphide is monoclinic with probable space group $P2_1/c$ and unit cell dimensions of $a = 5{\cdot}742(9)$, $b = 5{\cdot}794(2)$, $c = 5{\cdot}837(0)$ A., $\beta = 112{\cdot}91(9)°$.[493] From v.p. measurements[505] the heat of reaction for equation (51):

$$(51)\qquad RhP_2(s) + P(\text{white}) \rightarrow RhP_3(s) \qquad \Delta H = -11 \text{ kcal.}$$

was calculated. Rhodium diphosphide has *d* 5·88 g./c.c. and molecular volume 28 c.c.[505] It reacts vigorously with hot concentrated acids.[505]

Rhodium triphosphide, a grey-black compound, has *d* 5·16 g./c.c. and molecular volume 38·66 c.c. Its crystal structure is of the cobalt triarsenide type with $a=7{\cdot}966$ A.[508, 506] From v.p. measurements the heats of disproportionation for equations (52) and (53) were calculated.[505] Reaction with hot concentrated acids is vigorous.[505]

$$\left.\begin{array}{lll} (52) & 2RhP_3(s) \rightarrow 2RhP_2(s) + P_2(g) & \Delta H = 54 \text{ kcal.} \\ (53) & 4RhP_3(s) \rightarrow 4RhP_2(s) + P_4(g) & \Delta H = 60 \text{ kcal.} \end{array}\right\} t \sim 1000°\text{C.}$$

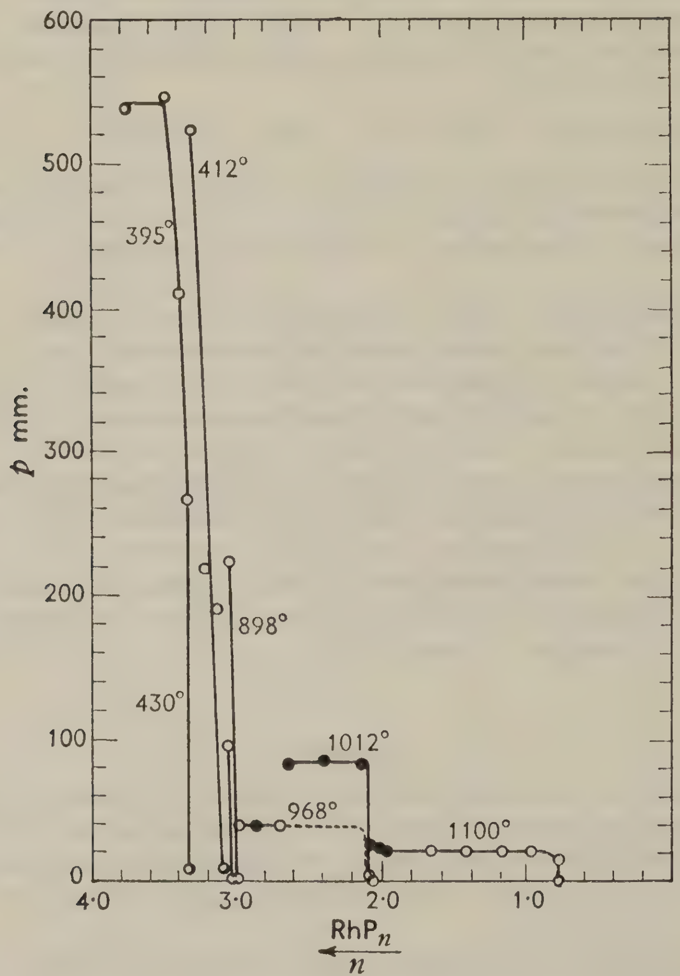

FIG. 33.—Vapour pressure analysis of rhodium phosphides

The depression of the m.p. of rhodium by phosphorus has been studied.[509]

Two ternary rhodium compounds with a cobaltite-type (CoAsS) structure have been described. RhPS has the unit cell dimension $a=5{\cdot}640$ A., and RhPSe, which has a superstructure of the pyrite (e.g. ullmannite) type, has $a=5{\cdot}795$ A.[569]

## Palladium

All of the known phosphides of palladium have been prepared by heating palladium with red phosphorus in evacuated sealed tubes.[510–1] In one preparation the elements were heated at 450° to 550°C. for several hours and then at 600° to 700°C. for 24 hr. The phase diagram is shown in Fig. 34.[510] Pentapalladium phosphide is the average composition of a homogeneous range.[510] It has now been established that this phase has the composition $Pd_{4\cdot8}P$.[661] It forms monoclinic crystals of space group $P2_1$, with $a=5{\cdot}004$, $b=7{\cdot}606$, $c=8{\cdot}416$ A., $\beta=95{\cdot}63°$. The structure in some ways resembles that of tri-iron carbide.[662] Tripalladium phosphide is orthorhombic and of the cementite type[510, 512, 572] with $a=5{\cdot}947$, $b=7{\cdot}451$, $c=5{\cdot}170$ A.,[513] $a=5{\cdot}18$, $b=6{\cdot}00$, $c=7{\cdot}46$ A.[572] and $a=5{\cdot}166$, $b=5{\cdot}971$, $c=7{\cdot}445$ A.[511] The composition is not constant, the homogeneity range varying from $Pd_3P_{0\cdot 75}$ to $Pd_3P_{1\cdot 0}$.[513] The lattice parameters for the phosphorus-rich limit are $a = 5\cdot 980$, $b = 7\cdot 440$, $c = 5\cdot 164$ A. and for the palladium-rich limit are $a = 5\cdot 645$, $b = 7\cdot 558$, $c = 5\cdot 071$ A.[513] Changes in the unit cell dimensions are explained by gaps in the space lattice due to lack of phosphorus atoms when $P < 8\cdot 83\%$ and by interstitial insertion of phosphorus atoms when $P > 8\cdot 83\%$.[514] Although all of the lattice parameters vary only one, $a = 5\cdot 166$ A., shows a sharp change at the stoicheiometric composition.[514] Tripalladium phosphide exhibits superconductivity, with a transition temperature of 0·75°K.[572] Pentapalladium diphosphide,[510] which is more probably heptapalladium triphosphide,[572] exists in two modifications, a high temperature form made by rapid quenching from 750°C. and a low temperature form made by annealing at 400°C. The high temperature form has a rhombohedral crystal lattice ($a = 7\cdot 28$ A., $\alpha = 110\cdot 12°$) and is a superconductor below 1·00°K., while the low temperature form is a superconductor below 0·70°K.[572] Palladium diphosphide, $PdP_2$, is monoclinic, $a = 6\cdot 207$, $b = 5\cdot 857$, $c = 5\cdot 874$ A., $\beta = 111\cdot 80°$[572, 663]; $a = 6\cdot 777$, $b = 5\cdot 856$, $c = 6\cdot 206$ A., $\beta = 126\cdot 42°$.[493] The electrical properties of palladium diphosphide and the corresponding ternary compound PdPAs have been determined.[660] Palladium phosphides are oxidized by air and the higher ones are hygroscopic.[510]

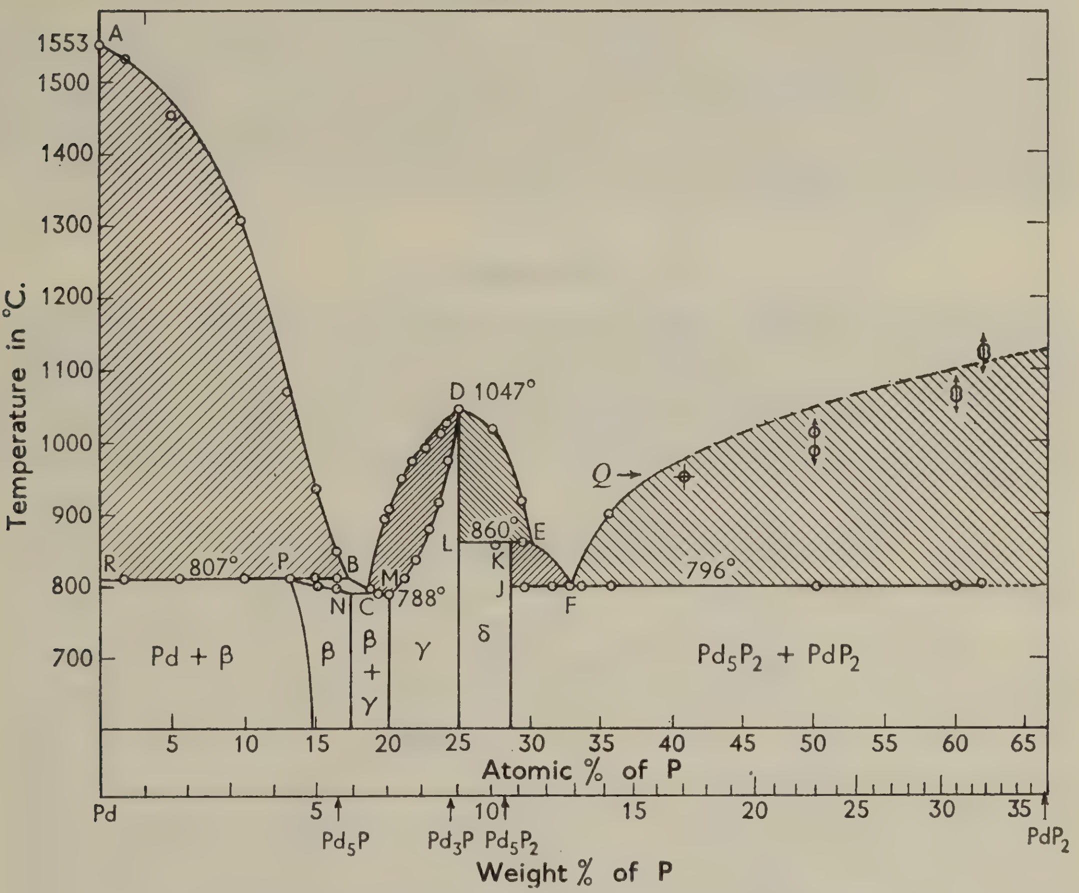

FIG. 34.—Phase diagram of the palladium–phosphorus system

## THE THIRD TRANSITION SERIES

### Lanthanum

At a temperature of 400° to 500°C., in a sealed tube, lanthanum reacts violently with red phosphorus to form lanthanum monophosphide.[515] This phosphide has also been obtained by fusion of stoicheiometric quantities of the elements at 1450°C. in an argon atmosphere followed by slow cooling to 700° to 800°C.,[516] or by the action of phosphine on dilanthanum trioxide at 1300°C.[664] $X$-Ray studies have shown it to have a similar structure to those of cerium and praseodymium phosphides which have the sodium chloride type of structure. The unit cell dimension is reported as being $a=6{\cdot}01(3)$ A.,[517] $a=6{\cdot}016$ A.[664] or $a=6{\cdot}025$ A.[516] The compound is a dark grey powder $d_{\text{calc.}}$ 5·18 g./c.c., insoluble in alkalis, soluble in nitric acid, slowly soluble in hydrochloric acid or aqua regia, and sparingly soluble in sulphuric acid.[664] It is decomposed by atmospheric moisture with evolution of phosphine.[515]

### Hafnium

Monohafnium phosphide exists in two forms. $\beta$-HfP (like TiP and $\beta$-ZrP) has a hexagonal lattice[574] which is transformed to a face-centred cubic lattice on heating above 1600°C. *in vacuo*. Presumably the transformation to $\alpha$-HfP occurs with loss of phosphorus as in the case of $\alpha$-ZrP (q.v.),[570] although the stability of this phosphide is very high, resembling that of $ThP_{0\cdot7}$ or UP.[631] Hafnium diphosphide, $HfP_2$, has been described. It is orthorhombic, with $a=6{\cdot}467$, $b=8{\cdot}646$, $c=3{\cdot}497$ A.; a metallic conductor with a positive thermoelectric power.[637]

### Tantalum

Tritantalum phosphide has a $Ti_3P$ lattice with $a=10{\cdot}154$, $c=5{\cdot}012$ A. Ditantalum phosphide is orthorhombic, with $a=14{\cdot}419$, $b=11{\cdot}552$, $c=3{\cdot}399$ A. Pentatantalum tetraphosphide is also orthorhombic with $a=14{\cdot}420$, $b=11{\cdot}547$, $c=3{\cdot}400$ A. All have been made by rapidly heating in an argon arc furnace an alloy of the appropriate stoicheiometry, made from red phosphorus and the metal in a heated evacuated silica tube.[655, 685]

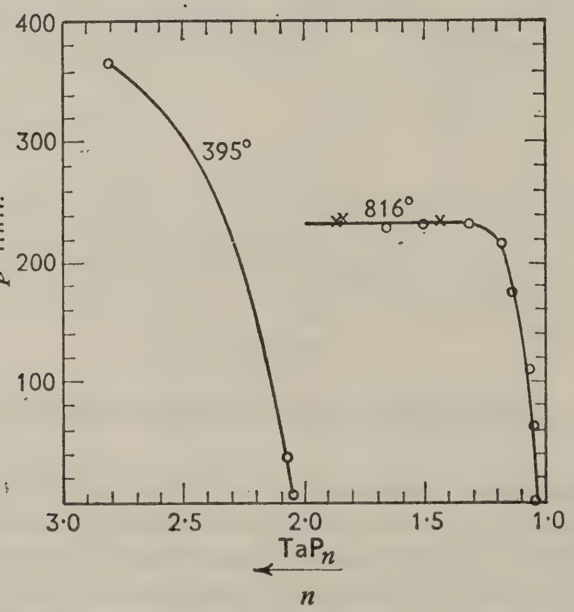

Fig. 35.—Vapour pressure analysis of tantalum phosphides

Monotantalum phosphide exists in two forms, $\alpha$-TaP and $\beta$-TaP which are prepared by heating tantalum diphosphide under high vacuum. Below 900°C. the $\alpha$-form is obtained and above 900°C. the $\beta$-form is produced.[518] Electrolysis of fused phosphate melts has also been shown to produce monotantalum phosphide,[304] as has the reaction of tricalcium diphosphide with tantalum metal.[566] In a comparison of vanadium, niobium and tantalum phosphides, it was suggested that the tantalum compounds are isomorphous with those of niobium.[305] This was confirmed for the $\alpha$ and $\beta$ forms of monotantalum phosphide both of which are greyish black with a metallic lustre.[292] The $\beta$-form has a NbAs lattice, with $a=3{\cdot}334$, $c=11{\cdot}377$ A.[655] and has a high thermal stability.[631] V.p. measurements (shown in Fig. 35[518]) enabled the heat of reaction for equation (54) to be calculated:

$$(54) \qquad TaP(s) + P(white) \rightarrow TaP_2(s) \qquad \Delta H = -12 \text{ kcal.}$$

Both the $\alpha$ and $\beta$ modifications are very resistant to chemical attack. Nitric acid and alkali react only at elevated temperatures and appreciable reaction is only obtained by alkali fusion with oxidizing agents.[518]

Heating the metal with excess of red phosphorus or a mixture of phosphine and hydrogen gives tantalum diphosphide.[518, 292] Fig. 35 shows the results of a tensimetric analysis from which equation (55) was established[518]:

$$(55) \qquad 4TaP_2(s) \rightarrow 4TaP(s) + P_4(g) \qquad \Delta H = +61 \text{ kcal.}$$

Tantalum diphosphide has similar chemical properties to the monophosphide and both phosphides are classed as hard metals.[518] The diphosphide has a monoclinic structure with $a = 8{\cdot}8608$, $b = 3{\cdot}2677$, $c = 7{\cdot}4882$ A., $\beta = 119{\cdot}308°$.[655] It is a metallic conductor, with a positive thermoelectric power.[637]

Crystal data have been determined for the ternary phosphides TaFeP, TaCoP, TaNiP.[653]

## Tungsten (Wolfram)

Electrolysis of lithium and sodium metaphosphate melts containing oxides of tungsten gave a cathodic product which analysis showed to be tetratungsten phosphide.[519] The reaction appears to depend on the formation of phosphine and hydrogen at the cathode. The density of this phosphide is 16·03 g./c.c. and it is decomposed irreversibly at 500° to 550°C. into ditungsten phosphide and $\alpha$-tungsten. Chemically it is not very reactive, since concentrated sulphuric acid reacts slowly whilst nitric acid, hydrochloric acid, and alkali do not attack it. Alkaline hydrogen peroxide produces phosphates and tungstates.[519] Other workers[315] suggest that tetratungsten phosphide is unstable and that it decomposes to give monotungsten phosphide rather than ditungsten phosphide.

Tritungsten phosphide has been prepared by the fused-salt method and identified by means of its $X$-ray diffraction pattern.[311–2] It has also been obtained by rapid chilling of a melt from an argon arc furnace. It appears to be metastable below 1000°C.[655]

The preparation of ditungsten phosphide has been accomplished by the Andrieux method of electrolyzing fused phosphate melts.[9, 10, 520] One of these products[520] has, however, been shown by $X$-ray methods to correspond to monotungsten phosphide.[315]

Monotungsten phosphide is obtained by the above method,[9–10, 311–2] by causing tricalcium diphosphide to react with tungsten or tungsten chloride,[566] or by heating the metal with red phosphorus in a silica tube.[313] It is isomorphous with the corresponding manganese, iron, cobalt and chromium compounds.[292] $X$-Ray measurements have shown it to possess the MnP type of structure[313] which can be regarded as a distorted nickel arsenide type.[315] Its unit cell dimensions are $a = 5{\cdot}734$, $b = 3{\cdot}249$, $c = 6{\cdot}222$ A.[313] (see also reference 571); densities of 12·3 g./c.c.[315] and 11·7 g./c.c.[292] have been reported. V.p. measurements are shown in Fig. 36.[315] The thermal stability of tungsten monophosphide is relatively low.[631] It is a greyish black compound which is not attacked by water or dilute acids at room temperature.[292]

Attempts to prepare tungsten diphosphide by reaction of the elements at high temperatures were unsuccessful.[499] The method finally used was to cause $WO_3$ to react with red phosphorus for two days at 500°C. The product was purified by reaction with 10% by weight of phosphorus at 550°C. for 24 hr.[499] Other workers have claimed a synthesis from the elements.[315] Tungsten diphosphide disproportionates according to equation (56):

$$(56) \qquad WP_2(s) \rightarrow WP(s) + P(white) \qquad \Delta H = +12 \text{ kcal.}$$

Densities of 8·6 g./c.c.[499] and 9·17 g./c.c.[315] have been reported for this black compound which exists in two forms. The first ($\alpha$-$WP_2$) has a monoclinic structure similar

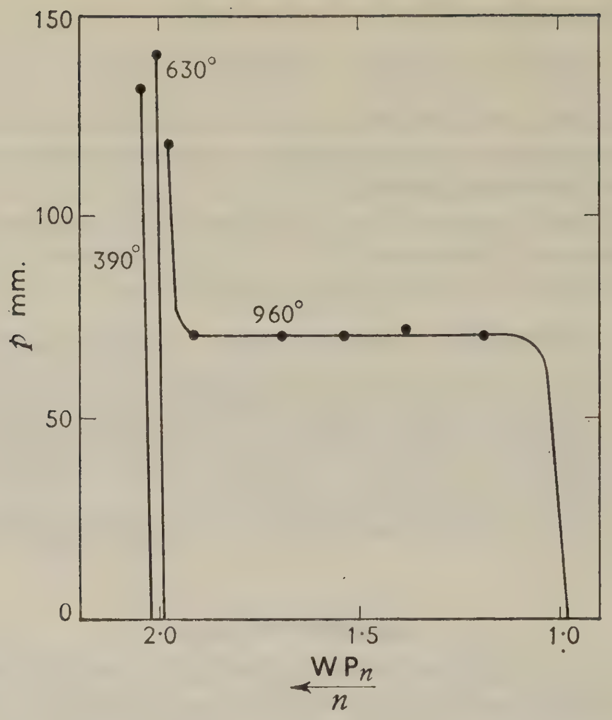

FIG. 36.—Vapour pressure analysis of tungsten phosphides

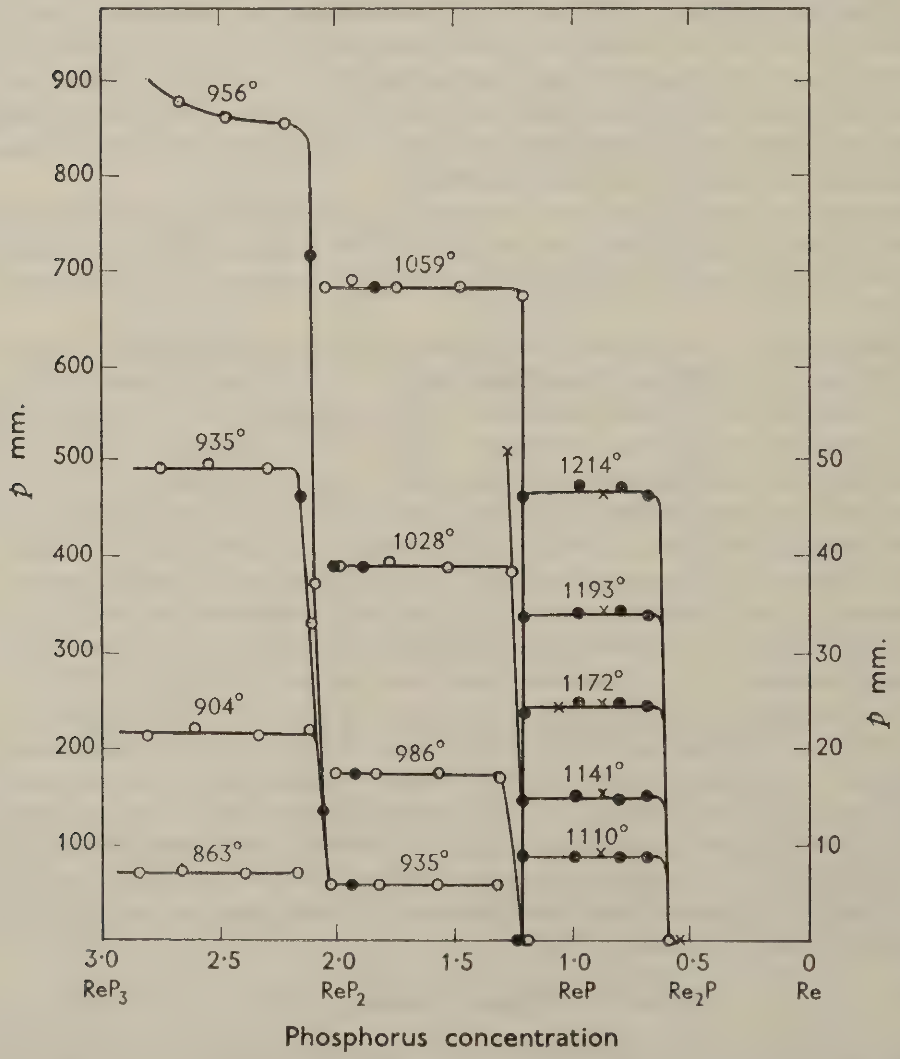

FIG. 37.—Pressure–concentration diagram for the rhenium–phosphorus system

to that of niobium diarsenide, with $a = 8{\cdot}5022$, $b = 3{\cdot}1695$, $c = 7{\cdot}4660$ A., $\beta = 119{\cdot}367°$.[637, 655] The second ($\beta$-$WP_2$) has an orthorhombic ($MoP_2$) structure with $a = 3{\cdot}166$, $b = 11{\cdot}161$, $c = 4{\cdot}973$ A.[571, 655] In its chemical properties $\beta$-$WP_2$ also resembles molybdenum diphosphide, since it is insoluble in concentrated hydrochloric acid or ammoniacal hydrogen peroxide, and is oxidized by concentrated sulphuric acid or aqua regia.[499]

The system tungsten–phosphorus–iron has been investigated up to 22% of phosphorus and 100% of tungsten.[457]

## Rhenium

The reaction of red phosphorus with rhenium was shown to commence at a temperature of approximately 750°C.[521] V.p. and *X*-ray measurements on the reaction product showed it to contain dirhenium phosphide, monorhenium phosphide, rhenium diphosphide and rhenium triphosphide. An *X*-ray determination of the structure of dirhenium phosphide has been made.[522] It is orthorhombic with $a = 5{\cdot}540$, $b = 2{\cdot}939$, $c = 10{\cdot}040$ A., space group *Pnma*. The calculated density is 16·4 g./c.c.[522] as compared with a previously measured density of 15·5 g./c.c.[521] The structure has been compared with that of diruthenium phosphide and the metal–metal distances are found to be shorter whilst the metal–phosphorus distances are longer.[522] The v.p. data shown in Fig. 37 enabled equations (57), (58) and (59) to be established[521]:

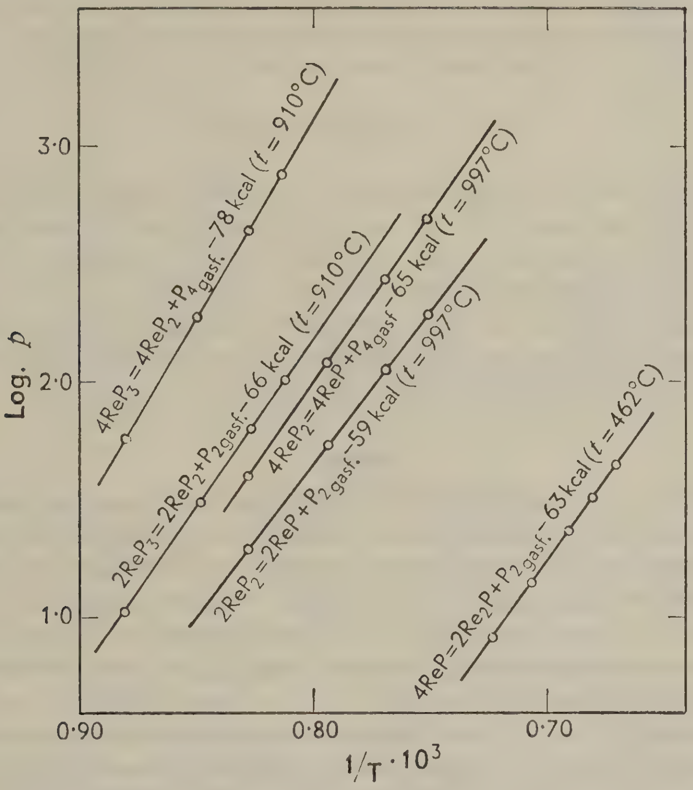

FIG. 38.—Decomposition pressure of rhenium phosphides

(57) For rhenium triphosphide $\log p_{(\text{mm.})} = -17060/T + 16{\cdot}77$

(58) For rhenium diphosphide $\log p_{(\text{mm.})} = -14220/T + 13{\cdot}37$

(59) For rhenium monophosphide $\log p_{(\text{mm.})} = -13780/T + 10{\cdot}90$

Heats of formation or disproportionation shown in Fig. 38 were calculated using the vapour pressure data. Densities and molecular volumes are collected together in Table VIII.[521] The molecular volumes are space additive. These phosphides react slowly with acids.[521]

*Table VIII.—Densities and Molecular Volumes for Rhenium Phosphides*

| Compound | Mol. vol. c.c. | $d_{25}$ g./c.c. |
|---|---|---|
| $Re_2P$ | 13·01 | 15·50 |
| ReP | 18·13 | 11·99 |
| $ReP_2$ | 28·06 | 8·83 |
| $ReP_3$ | 38·19 | 7·30 |

### Osmium

The system osmium–phosphorus has been studied[503] and only one phosphide, the diphosphide, recognized. Osmium and phosphorus when heated together at 1190°C. produce this phosphide which has a v.p. of only 8 mm. of mercury at this temperature. Its heat of formation from solid osmium and phosphorus gas is

$$\Delta H = -70 \text{ kcal./mole}^{503}$$

and its crystal structure is of the marcasite type with space group *Pnnm*.[504] This phosphide is a semiconductor having an energy gap of *ca.* 1·2 e.v. and a magnetic susceptibility, $\chi_{\text{mol}}$, of $-74 \times 10^{-6}$ c.g. units at 295°K.[573] Chemically it is very inert, air, acids and oxidizing agents having no effect upon it.[503]

A ternary compound, OsPAs, has been reported, also having a marcasite-type structure.[573] The semiconducting compounds OsPS and OsPSe, with an arsenopyrite structure, have also been described.[659]

### Iridium

Of the phosphides of iridium, the diphosphide has been prepared by heating iridium powder with red phosphorus for many hours, after which excess of phosphorus was distilled off.[523] The other phosphide, di-iridium phosphide can be obtained from this by heating at 1150°C. under reduced pressure. If the heating is prolonged for many hours the di-iridium phosphide gradually loses phosphorus.[523] The lower phosphide is a grey-blue compound having a m.p. of between 1310°C. and 1360°C. It has the anti-fluorite structure[507, 504] with $a = 5{\cdot}53(5)$ A. and a calculated molecular volume of 25·7 c.c.[507] Its resistance to chemical attack is greater than that of the diphosphide which is a deep black compound having *d* 9·15 g./c.c. and molecular volume 27·9 c.c. Iridium diphosphide is diamagnetic.[575] It is stable towards hydrochloric acid and nitric acid but is attacked by aqua regia, boiling concentrated sulphuric acid and a mixture of bromine and hydrochloric acid.[523] Iridium triphosphide is reported as having a structure of the skutterudite type with space group *Im*3.[504, 665]

Ternary compounds IrPS and IrPSe have been described. The sulphide has a cobaltite-type lattice, $a = 5{\cdot}650$ A. and the selenide a superstructure of the pyrite (ullmannite) type, with $a = 5{\cdot}798$ A.[569]

### Platinum

Platinum has been heated in phosphorus vapour in a closed quartz tube to give platinum diphosphide for *X*-ray studies.[524] The only other investigation was a thermal, *X*-ray and tensimetric analysis of the platinum–phosphorus phase system which is shown in Fig. 39.[525] Although it is not shown in the figure platinum diphosphide has m.p. above 1500°C. Its crystal structure is cubic with $a = 5{\cdot}683 \pm 0{\cdot}004$ A.,[524] $a = 5{\cdot}6956 \pm 0{\cdot}0005$ A.[666–7] Its electrical properties and those of the isomorphous PtPAs have been recorded.[660] The oxidation of phosphorus by steam has been catalyzed by platinum diphosphide.[74] An unusual compound, $Pt_{20}P_7$, is important because of its low m.p. and the ease with which it can be formed. It has

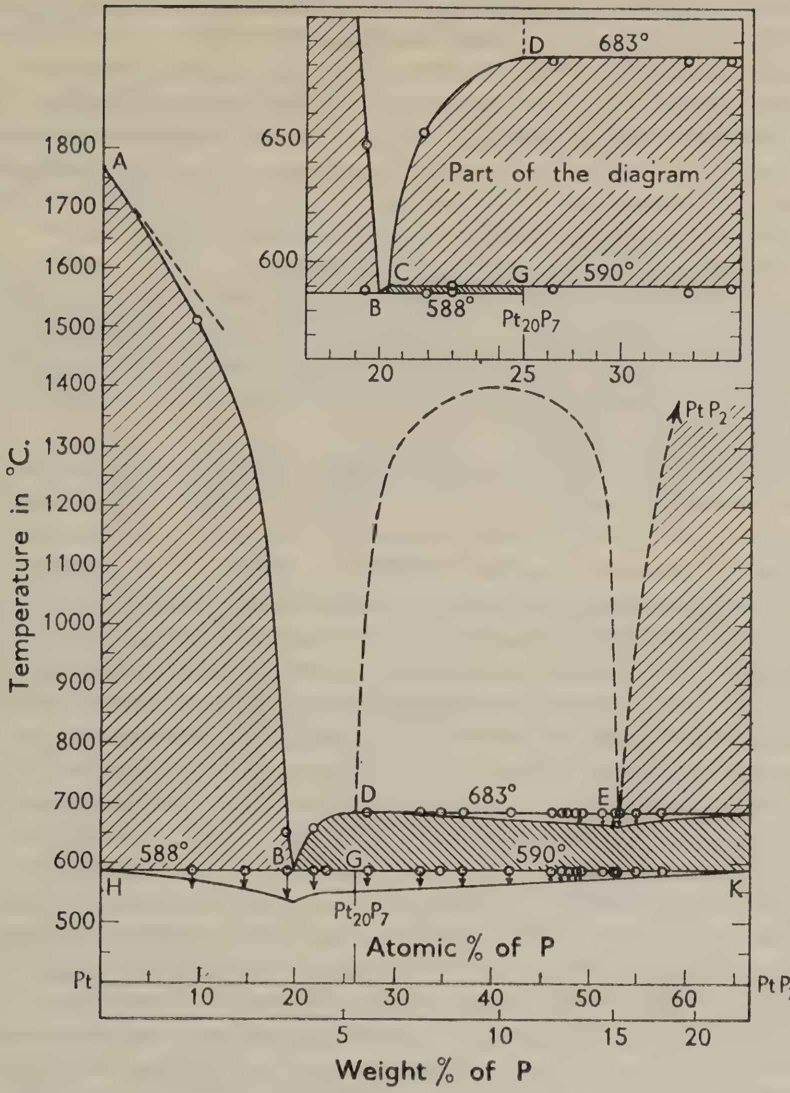

FIG. 39.—Phase diagram of the platinum–phosphorus system

been shown to have no superconducting properties at temperatures down to 0·35°K.[572] Care has to be taken in the use of platinum apparatus when phosphorus is likely to be present.[525–7]

## The Rare Earths

In this group, the phosphides of general formula MP (where M is the rare earth metal) have been prepared by heating phosphorus with the rare earth metal in a sealed tube or in argon atmosphere at elevated temperatures. The unit cell dimensions and magnetic susceptibilities of a series of rare earth monophosphides have been reviewed.[547] The magnetic properties of the series of phosphides GdP–ErP are determined largely by the crystal structure and lattice spacings.[672] The Fermi momentums $k_F$ of the conduction electrons have been calculated from the paramagnetic Curie temperatures and the lattice spacings of a series of rare earth phosphides.[668]

Cerium reacts violently with phosphorus at 400° to 500°C.[515] The monophosphide has a sodium chloride type of structure with $a = 5{\cdot}89(7)$,[517] 5·909 A.[516] Its magnetic properties have been determined over the range 4–300°K.[669] Heating cerium phosphide in air causes only slight oxidation and it is probably the most stable rare earth phosphide known, though it evolves phosphine when treated with water.[515]

Praseodymium monophosphide was prepared as above.[515] It too has the sodium chloride type of structure with $a = 5{\cdot}86(0)$,[517] 5·87(2) A.,[516] is oxidized slowly in the atmosphere and liberates phosphine when treated with water.[515] Its magnetic properties between 4 and 300°K. have been reported.[669]

Neodymium monophosphide is formed by a vigorous reaction between the elements at 400° to 500°C.,[528] or by passing phosphine over $Nd_2O_3$ at 1300–1350°C. or over neodymium metal at 1000–1100°C.[670–1] The compound is a black powder, insoluble in water or alkalis, but soluble in acids, and reacting violently with nitric acid.[671] It has the sodium chloride structure with $a = 5{\cdot}82(6)$,[528] 5·838,[516] 5·843 A.[671] and is unstable, liberating phosphine when attacked by moist air.[528]

The reaction of samarium with phosphorus is slow, but a pure product can be obtained by pulverizing the product and reheating.[529] The phosphide can also be prepared by passing phosphine over samarium oxide at 1300–1350°C. or over the metal at 900–950°C. Samarium phosphide is readily soluble in nitric acid.[670] It has a sodium chloride type of structure with $a = 5{\cdot}760$ A.[529] Magnetic susceptibility measurements show that at 289°K. $\chi \times 10^3 = 1{\cdot}1$.[530]

Europium monophosphide is reported briefly to have a cubic lattice.[654]

Gadolinium monophosphide has been prepared by treating gadolinium chips in evacuated quartz tubes with phosphorus vapour, then compressing the material which is heated *in vacuo* or in argon at 1100° to 1400°C.[516] As with other rare earth phosphides it has a sodium chloride type of structure with $a = 5{\cdot}723$ A.[516] Magnetic susceptibility measurements[530] indicate that it conforms to the Curie–Weiss law.[326] It has a moment of 7·9 Bohr magnetons corresponding to $Gd^{3+}$ and $\chi \times 10^3$ at 298°K. is 28·5.[530] The induced ferromagnetism of GdP has been studied.[688]

Terbium monophosphide, as prepared by heating the elements *in vacuo* at 300° to 600°C., pressing, and then heating for some hours at 1100° to 1300°C. is dark grey and has the sodium chloride type of structure with $a = 5{\cdot}688$ A. It conforms to the Curie–Weiss law[326] in the range 73° to 473°K. and $\chi \times 10^3$ at 298°K. is 39·5.[531]

Dysprosium monophosphide has been synthesized by heating the metal with phosphorus at 550°C. for 5–7 days followed by compression of the powder and further heating at 1100° to 1300°C. until the reaction is complete. It has the sodium chloride type of structure and magnetic susceptibility measurements show that it follows the Curie–Weiss law[326] down to approximately 100°K. It has a paramagnetic Curie point ($\theta p$) of 6°K.[576] The magnetic moment indicates the presence of $Dy^{3+}$.[532]

The synthesis of holmium monophosphide has been accomplished by heating the elements together in an evacuated tube at 1100° to 1400°C. It is grey, has the sodium chloride type of structure with $a = 5{\cdot}626$ A. and a magnetic susceptibility of 0·0461,[533] with a Curie point of 4·2°K.[576]

Erbium monophosphide was synthesized by heating the metal in phosphorus vapour at 500° to 800°C. and finally at 1100°C. for 1 hr. It has the sodium chloride type of structure and magnetic susceptibilities showed it to follow the Curie–Weiss law[326] at low temperatures. Magnetic moment measurements indicate that the structure contains $Er^{3+}$ ions.[534]

Ytterbium monophosphide is reported to have a cubic lattice,[654] as have the monophosphides of thulium ($a = 5{\cdot}573$ A.) and lutetium ($a = 5{\cdot}533$ A.). Curie temperatures, magnetic susceptibilities and magnetic moments have been recorded for the latter two phosphides.[673]

## THORIUM, URANIUM AND TRANS-URANIC ELEMENTS

### Thorium

Two phosphides of thorium have been prepared. Trithorium tetraphosphide has been obtained by passing phosphine over the heated hydride[535–7] and by heating thorium metal in phosphorus vapour.[306, 538] This phosphide has a body-centred cubic structure with $a = 8{\cdot}624 \pm 0{\cdot}020$ A.,[535] $a = 8{\cdot}600 \pm 0{\cdot}002$ A.,[539] $d$ 8·44 g./c.c.[538] Values for the thermoelectric power and electrical conductivity up to 950°C. have been given.[674] It liberates phosphine when treated with dilute acids but is unattacked by cold water and heating to 1100°C. has no effect upon it.[538]

By heating trithorium tetraphosphide at 1100–2400°,[634, 675] or by heating thorium with phosphorus,[539, 675] or trithorium tetraphosphide,[675] a new cubic phase of variable composition is formed, approximating to thorium monophosphide. The lattice dimensions are a linear function of composition from $ThP_{0\cdot55}$ ($a = 5\cdot830$ A.) to $ThP_{0\cdot96}$ ($a = 5\cdot840$ A.) (cf. $a = 5\cdot818$ A.[539]). Thermodynamic information has been obtained for the system by experiments on high-temperature solid electrochemical cells. These showed that for the reaction:

$$Th + Th_3P_4 \rightarrow 4ThP$$

at 1173°K. the free energy change is $-53\cdot7 \pm 2\cdot8$ kcal./g. atom Th, the entropy change $-9\cdot3 \pm 3\cdot7$ g.-cal./mole, and the enthalpy change $-64\cdot6 \pm 7\cdot1$ kcal./g. atom Th. Hence free energies of formation at 1173°K. were deduced for ThP ($-71\cdot5$ kcal./deg. mole) and $Th_3P_4$ ($-232$ kcal./mole), while the enthalpy of formation of ThP at the same temperature is $-106$ kcal./mole.[676] Thorium monophosphide which does not melt up to 2400°C. is a blue substance possessing great chemical resistance.[675] The chemical analysis of the thorium phosphides has been discussed.[677]

### Uranium

Monouranium phosphide, triuranium tetraphosphide and uranium diphosphide were all prepared by reaction of the elements at elevated temperatures,[540, 581, 678] whilst diuranium triphosphide has been prepared by the reaction of uranium hydride with phosphine.[541] A patent dealing with the preparation of uranium phosphide from the hydride and phosphine has been granted.[542] All of the phosphides are grey. Uranium monophosphide has a cubic face-centred structure with $a = 5\cdot589$ A.,[543, 679] and a molecular volume of 27 c.c.,[540] triuranium tetraphosphide is structurally similar to the thorium compound with $a = 8\cdot19(7)$ A.[543] and molecular volume 35 c.c.,[540] whilst uranium diphosphide is structurally similar to $UAs_2$ with cell dimensions for the tetragonal unit cell $a = 3\cdot800$ and $c = 7\cdot762$ A.[581] The magnetic properties of the three phosphides have been studied, triuranium tetraphosphide being ferromagnetic, and the others antiferromagnetic.[680] The thermoelectric power and electrical conductivity of uranium monophosphide[681] and triuranium tetraphosphide[682] have been determined. From tensimetric measurements shown in Fig. 40 equations (60) and (61) were established:

$$(60) \qquad 6UP_2(s) \rightarrow 2U_3P_4(s) + P_4(g) \qquad \Delta H = +52 \text{ kcal.}$$

$$(61) \qquad \tfrac{1}{2}U_3P_4(s) + P(\text{white}) \rightarrow \tfrac{3}{2}UP_2(s) \qquad \Delta H = -10 \text{ kcal.}$$

Triuranium tetraphosphide is the most reactive of these phosphides and produces phosphine when treated with hydrochloric acid. Uranium monophosphide is inert to atmospheric moisture and is also resistant to oxidation,[679] probably because of the formation of a protective surface layer of amorphous uranyl phosphate.[683] Uranium diphosphide, the least reactive, is not attacked by dilute hydrochloric acid but dissolves in nitric acid.[540]

### Neptunium

Neptunium, heated with excess of red phosphorus in an evacuated, sealed quartz tube at 750°C. for 16 hr. gives a product trineptunium tetraphosphide which is isomorphous with the corresponding thorium compound.[544] It is unaffected by water but a vigorous reaction, probably represented by equation (62), takes place with hydrochloric acid[544]:

$$(62) \qquad Np_3P_4 + 12HCl \rightarrow 3NpCl_4 + 4PH_3$$

### Plutonium

Plutonium monophosphide is formed by reaction of the elements *in vacuo* or helium[545, 580] or from plutonium trihydride and phosphine at 400–600°C. followed

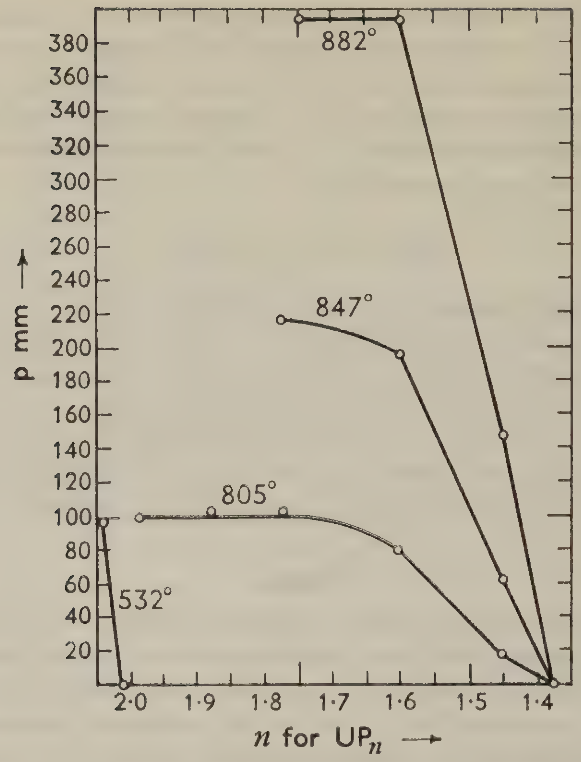

FIG. 40.—Vapour pressure analysis of the higher uranium phosphides

by tempering at 1400°C. *in vacuo*.[684] The phosphide is dark grey, and decomposes at 2600°C. and 2 atm. pressure. It is reported to have a cubic structure with $a$ = 5·644 ± 0·004 A., $d$ = 9·87 g./c.c.[545] or $a$ = 5·6598 A., $d_{\text{calc.}}$ = 9·893 g./c.c.[684]

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## SECTION VIII

# PHOSPHIDES OF NON-METALS

BY A. WILSON AND N. L. PADDOCK

## GROUP 0

### Helium

Helium is the only rare gas for which any evidence of reaction with phosphorus has been reported. At liquid-air temperatures and under the influence of electron bombardment, helium is absorbed by, or forms an interstitial compound with, phosphorus. The product decomposes suddenly at $-125$°C. with evolution of helium. The vapour pressure is of the order 0·0005 mm. Hg at $-185$°C.[112]

## GROUP 3

### Boron

When boron monophosphide, BP, is decomposed by heating it to a temperature between 1000° and 1700°C. in an inert atmosphere, the compound tridecaboron diphosphide is formed.[1, 117–20, 122] Tridecaboron diphosphide is also formed when aluminium monophosphide is caused to react with amorphous boron[1] or boron trichloride[105] under similar conditions. *X*-Ray data show that the crystalline compound has rhombohedral symmetry with $a = 5{\cdot}984$ and $c = 11{\cdot}850$ A.[2]; other workers give $a = 5{\cdot}231$ A., $\alpha = 69{\cdot}50°$.[105] The space group is probably $R\bar{3}m$ since the compound is isomorphous with $B_4C$ and $B_4Si$. This *X*-ray work gives *d* $2{\cdot}74 \pm 0{\cdot}02$ g./c.c.,[1] 2·76 g./c.c.[105] The electrical conductivity of tridecaboron diphosphide has been recorded.[119] Other less well-defined phosphides containing higher proportions of boron, and made in similar manner, have been described.[106, 119]

If boron monophosphide, at a pressure of approximately 1 mm. of mercury, is heated to a temperature above 1100°C. it decomposes and hexaboron monophosphide is formed.[3, 106] Using the appropriate data, $\Delta H^\circ_{298°\text{K.}} = -31{\cdot}0$ kcal./mole has been calculated for the reaction:

$$6B(\text{cubic}) + P(\text{white}) \rightarrow B_6P$$ [4]

Hexaboron monophosphide has a hardness of 9·0–9·7 on Mohs' scale, and *d.* 2·45 g./c.c. It is stable at 2000° in air.[107, 121] This compound is extremely inert chemically and elevated temperatures are required for attack by alkali, whilst temperatures of 500° and 800°C. are required for attack by chlorine and oxygen, respectively.[3] There is some doubt as to whether hexaboron monophosphide exists or whether it is identical with tridecaboron diphosphide.[2] Other investigators using implosive shock techniques were unable to prepare this phosphide,[5] but an *X*-ray examination should either confirm or disprove its existence, e.g. [121].

Boron monophosphide has been studied to some extent because of its semiconducting properties. Much of this work belongs to the realm of physics and a comprehensive survey of these properties has been given in more appropriate places.[6–8]

Direct reaction of boron and red phosphorus at temperatures between 1000°C. and 1100°C. produces boron monophosphide.[3, 9–11, 122–5] The reaction shows three regions of kinetics, at 1000–1150°; a 'kinetic' phase in which the reaction is of the second order in $P_2$ and independent of the boron concentration, a transitional phase, and a 'diffusion' phase (first order in $P_2$).[125] At temperatures up to 1350°C., under pressures of 9000–15,000 kg./cm.$^2$, cubic boron monophosphide is formed,[126] while some tridecaboron diphosphide is formed at 100 atm. and 1600°C.[127] It has also been prepared by heating the addition compounds of boron trichloride with phosphorus pentachloride, and of boron tribromide with phosphine, to 300°C. in sealed tubes.[12, 3] The product obtained by the decomposition of the boron trichloride–phosphorus pentachloride complex varied in composition between boron monophosphide and pentaboron triphosphide but no evidence for the latter compound was found.[3] Boron monophosphide is also formed by passing boron trichloride over aluminium monophosphide heated to 1000°C.,[3] or zinc phosphide heated to 900–1085°C.,[118, 128] by carbon reduction of a borate–phosphate mixture dissolved in a sodium chloride melt at 480–1820°,[108] or by the reaction of boron trichloride, hydrogen and phosphorus at 1000°C.[3, 118] This last method is said to give the purest product.[3] Boron tribromide has been used in place of boron trichloride.[129] Although the material, as prepared, is usually amorphous, it can be crystallized by heating to over 1400°F. in phosphorus vapour[13, 130]; the volatility is enhanced by the addition of a trace of iodine to the system.[131] The crystalline material has the cubic zinc-blende type structure with $a = 4{\cdot}55$,[9] 4·538,[10, 11] 4·537,[14] 4·547 A.,[13] $d$ 2·94 g./c.c.[109] It is extremely hard and by analogy with boron nitride and carbon it was expected to be harder than silicon carbide[9] but this appears not to be borne out by experiment.[14–5] Although material produced so far is impure by semiconductor standards, indications are that it may prove to be useful in this application and this, together with its possible use as an abrasive, has led to methods of manufacture being patented.[13–4, 16–22, 123–4, 132] The electrical resistivities of boron–phosphorus alloys are shown in Fig. 1.[23] A single crystal of boron monophosphide, prepared by vacuum sublimation, had a thermal e.m.f. of 260 $\mu$v/°C. at 20–150°C. and a microhardness of 4000 kg./mm.$^2$,[130] The infra-red dielectric constant and the ultra-violet optical properties of the phosphide have been determined.[134] Thermodynamic studies have been made on certain equilibria. For equation (1):

$$(1) \qquad BCl_3 + \tfrac{3}{2}H_2 + \tfrac{1}{4}P_4 \rightleftharpoons BP + 3HCl, \qquad T = 1193°\text{–}1543°\text{K.}$$

the equilibrium constant is given by equation (2):

$$(2) \qquad \log K = 1{\cdot}377 - 1550/T$$

From this there were obtained: $\Delta H° = 7090$ g.-cal., $\Delta S° = 6{\cdot}30$ g.-cal./degree, and $\Delta G° = -1730$ g.-cal. (all mole$^{-1}$) at 1400°K.[4] Using the above data and literature values, $\Delta H^{\circ}_{298°\text{K.}} = -19{\cdot}90$ kcal./mole was calculated for the reaction given in equation (3):

$$(3) \qquad B(\text{cubic}) + P(\text{white}) \rightarrow BP(\text{cubic})$$

Also for the reaction shown in equation (4) the following data were obtained: $\log K = 3{\cdot}134 - 5900/T$, $\Delta H° = 27{,}000$ g.-cal., $\Delta S° = 14{\cdot}34$ g.-cal./degree, and $\Delta G°$ at 1500°K. = 5480 g.-cal. (all mole$^{-1}$)

$$(4)^4 \qquad BP \rightleftharpoons \tfrac{1}{6}B_6P + \tfrac{5}{12}P_2, \qquad T = 1473\text{–}1573°\text{K.}$$

A 'third law' calculation using estimated entropies and heat capacities gave a heat of dissociation at 298·16°K. of 73·2 kcal./mole of $P_2$(g) for equation (5):

$$(5)^{24} \qquad \tfrac{26}{11}BP(s) \rightarrow \tfrac{2}{11}B_{13}P_2(s) + P_2(g)$$

A heat of formation for gaseous boron monophosphide of 62 kcal./mole was estimated using oxide systems as a guide,[25] while the heat of formation of the solid monophosphide at 1200°C. has been estimated as $99{\cdot}6 \pm 0{\cdot}3$ kcal./mole.[129] From observations of *K*-emission line shifts it was concluded that the compound has a strong ionic component.[26] The dependence of vapour pressure on temperature can be expressed as in equation (6):

$$(6) \qquad \log p_{(\text{mm.})} = -13{,}700/T + 10{\cdot}1$$

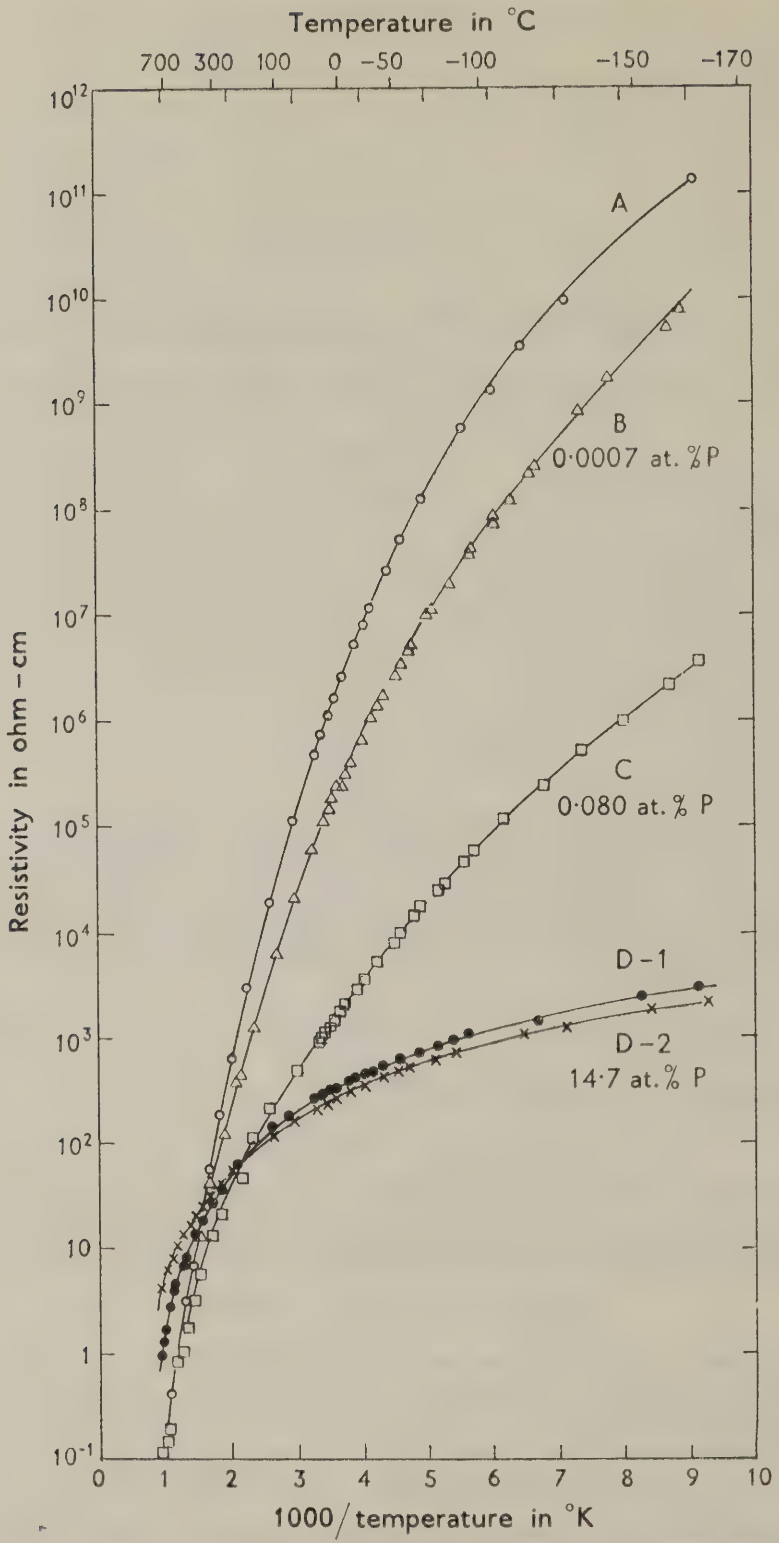


FIG. 1.—Resistivity of boron and boron–phosphorus alloys as a function of the reciprocal of the absolute temperature

Boron monophosphide, like the other boron phosphides, is extremely resistant to chemical attack[3, 118, 133] although molten alkali, oxygen at 800°C. and chlorine at 500°C. show some reaction.[3] When it is heated in air there are no signs of decomposition at 1000°C.[12]; it does not burn at 1200°C.[14] and it is resistant to decomposition even at 5400°F.,[13] though this is probably due to the formation of inert oxide layers. No signs of decomposition are apparent at 1250°C. in phosphorus vapour.[10] It is resistant to hydrolysis[12] and acids[13–4] and it is necessary to heat it to 800°C. before it will react with ammonia to produce phosphine and cubic boron nitride.[12]

A material containing boron and phosphorus in equal atomic proportions has been prepared in a series of high pressure, high temperature studies. At a pressure of 94,500 atm. and a temperature of 2500°C. boron and phosphorus react to give a black, soft material which is a moderately good conductor of electricity. It has a face-centred cubic structure with $a = 4{\cdot}54$ A.[27]

A patent has been granted for the stabilization of a material having composition $B_3P_4$ against oxidation in the region of 2000° to 2500°F. Stabilizers include boron as well as oxides of sodium, potassium, magnesium and beryllium.[28]

Ternary systems investigated are Fe–P–B, Cr–P–B, Mn–P–B, Co–P–B and Ni–P–B.[29, 135–6] In the Fe–P–B system two ternary phases exist. These are $Fe_5PB_2$ and $Fe_3P_{1-x}B_x$; the latter is homogeneous in the approximate range $0{\cdot}48 < x < 1$ at 1000°C. $Fe_3P_{0\cdot37}B_{0\cdot63}$ crystallizes in the space group $P4_2/n$ with $a = 8{\cdot}812$, $c = 4{\cdot}375$ A. $Fe_5PB_2$ crystallizes in the space group $I4/mcm$ with $a = 5{\cdot}482$, $c = 10{\cdot}332$ A.[29] In the Mn–P–B system a ternary phase $Mn_5PB_2$ exists which is isostructural with $Fe_5PB_2$, whilst in the Co–P–B system three ternary phases exist. $Co_3P_{1-x}B_x$ is homogeneous in a narrow range near $x = 0{\cdot}7$, $Co_3P_{1-y}B_y$ is homogeneous near $y = 0{\cdot}5$ and $Co_5PB_2$ is isostructural with $Fe_5PB_2$ and $Mn_5PB_2$.[29]

## GROUP 4

### Carbon

Although no crystalline phosphides of carbon stable at room temperature exist, spectra observed when an electrical discharge was passed through a mixture of argon and phosphorus vapour were thought to be due to a species carbon monophosphide[30] arising apparently from tap grease or sealing wax. Wave numbers have been calculated for this compound[31] and a complete vibrational–rotational analysis of the band system between 2900 and 4400 A. has been carried out.[32] A heat of formation of 74 kcal./mole was estimated using oxides as a guide[25] and tables of $(G° - H°)/T$, $S°$, $C_p^{\circ}$ include values for CP.[33] These values at 273·15°K. are:

$$-(G° - H°)/T = 44{\cdot}064 \text{ g.-cal. deg.}^{-1} \text{ mole}^{-1}$$
$$S° = 51{\cdot}038 \text{ g.-cal. deg.}^{-1} \text{ mole}^{-1}$$

and

$$C_p^{\circ} = 7{\cdot}090 \text{ g.-cal. deg.}^{-1} \text{ mole}^{-1}$$ [33]

It is reported that an amorphous yellowish compound, $P_2C_6$, is obtained when an ether solution of phosphorus trichloride is caused to react with magnesium acetylene iodide at room temperature. It is insoluble in ordinary solvents, is not attacked by acids or alkalis and ignites when slightly heated, burning to $P_2O_5$ without the liberation of carbon.[113]

Some work has been done on the carbon–phosphorus–iron system[34–6] and the carbon–phosphorus–iron–silicon system.[36] It is thought that in the low phosphorus range the carbon–phosphorus–iron system may be similar to the carbon–silicon–iron system.[37]

### Silicon

Mixtures of monosilane and phosphine in the ratio 1:1 or 1:2 give as product disilicon monophosphide when heated at 450°C. under a total pressure of 200 mm. of mercury.[38] It is a blue-black amorphous solid which decomposes when heated to 600°C. giving silicon and silicon monophosphide.[38]

The above work supports earlier evidence for the existence of silicon monophosphide which was prepared by heating together silicon and phosphorus at high temperatures.[39] A heat of formation of 80 kcal./mole has been estimated for this compound[25] which, if heated to above 1000°C., decomposes according to equation (7)[39]:

$$(7) \qquad 4SiP(s) \rightarrow 4Si(s) + P_4(g), \quad \Delta H = 72 \text{ kcal.}, \quad t \sim 1100°C.$$

Its vapour pressure varies with temperature according to equation (8):

$$(8)^{39} \qquad \log p_{(\mathrm{mm.})} = -15{,}710/T + 13{\cdot}769$$

It crystallizes as needles having a density of 2·4 g./c.c. and is hydrolyzed by hot water.[40]

Silicon monophosphide was recognized in a study of the binary system silicon–phosphorus; the results are shown in Fig. 2.[40] Ternary systems which have been studied are silicon–phosphorus–copper,[41] silicon–phosphorus–iron[42–3] and silicon–phosphorus–aluminium.[44] A compound $CuSi_2P_3$ exists in the silicon–phosphorus–copper system. It belongs to a class of semiconductors of the general form $A^{I}B_2^{IV}C_3^{V}$ and has a distorted zinc-blende structure with $a = 5{\cdot}25$ A.[45] In the system silicon–phosphorus–iron a new compound $FeSi_4P_4$ was established.[43]

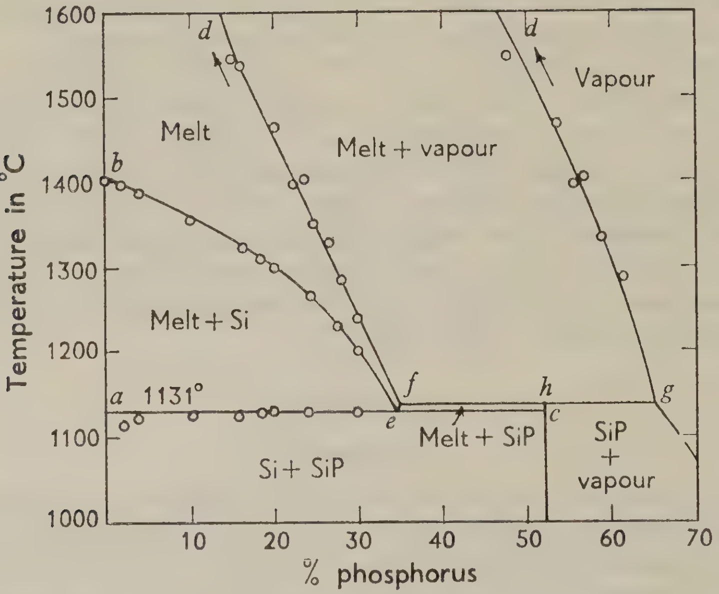


FIG. 2.—The silicon–phosphorus phase system

## Germanium

Germanium monophosphide was prepared by heating germanium with excess of phosphorus in an evacuated tube at 400°C. The product was identified by *X*-ray analysis and vapour pressure measurements. From the results shown in Fig. 3 the heats of formation according to equations (9) and (10) were calculated[46]:

$$(9) \qquad 4Ge(s) + P_4(g) \rightarrow 4GeP(s), \qquad \Delta H = -37 \text{ kcal.}; \qquad t = 540°C.$$

$$(10) \qquad Ge(s) + \tfrac{1}{4}P_4(\text{white}) \rightarrow GeP(s), \qquad \Delta H = -6 \text{ kcal.}$$

The free energy of formation of solid GeP from the gaseous elements has been estimated as $\Delta G_{T°K} = -17{,}900 + 11{\cdot}3\,T$ g.-cal. mole$^{-1}$ [110]

The semiconducting phosphides zinc germanium diphosphide, $ZnGeP_2$, and cadmium germanium diphosphide, $CdGeP_2$, have been discussed from a practical point of view.[47] They have the chalcopyrite type of structure with $a = 5{\cdot}46$ and $a = 5{\cdot}73_8$ A., respectively.[45] Other phosphides involving three elements are magnesium germanium diphosphide $MgGeP_2$ which has a zinc-blende structure with $a = 5{\cdot}65_2$ A.[45] and copper digermanium triphosphide, $CuGe_2P_3$. The last compound belongs to a new group of semiconductors of general formula $A^{I}B_2^{IV}C_3^{V}$ and has a disordered zinc-blende structure with $a = 5{\cdot}37_5$ A.[45] Germanium monophosphide, GeP, has been considered as a heat transfer fluid in atomic energy work.[48]

The binary system, germanium–phosphorus and the ternary system germanium–phosphorus–aluminium have been studied at low phosphorus concentrations.[44] The

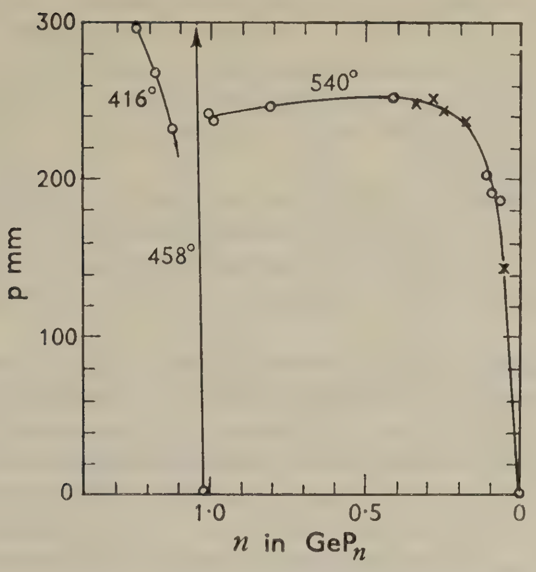


FIG. 3.—Vapour pressure analysis of the germanium–phosphorus system

ternary glasses $Ge_3PS_6$ and $Ge_7PS_{12}$ have good infra-red transmissivities in the 3–5μ region as well as low refractive indices.[137]

## GROUP 5

### Nitrogen

The existence of two nitrides of phosphorus, PN and $P_3N_5$, has been established; a third nitride, $P_4N_6$, has been reported, but there is some doubt about its individuality.

PHOSPHORUS NITRIDE (PHOSPHORUS MONONITRIDE)

Phosphorus nitride, PN, is formed from the elements, either thermally,[49] or under the influence of an electrical discharge.[50, 116] The thermal reaction requires a high temperature (1500° to 1800°) for the dissociation of the phosphorus molecule. On a tungsten surface above 1800° the rate of synthesis is proportional to the square root of the concentration of phosphorus,[51] the rate-determining step being the dissociation of the $P_2$ molecule, with an activation energy of 59 kcal./mole.

The diatomic product PN is thermodynamically unstable at lower temperatures, though it dissociates only slowly,[51] and may be trapped on relatively cool walls at 400° to 500° as a yellow, amorphous,[52] polymeric solid. The PN molecule was discovered in gas discharges through mixtures of nitrogen and phosphorus,[53] the frequencies of the series of band-heads in a system due to a $^1\Pi \rightarrow {}^1\Sigma$ transition being closely represented by

$$\nu(\text{cm.}^{-1}) = 39{,}699{\cdot}3 + (1094{\cdot}75v' - 7{\cdot}25v'^2) - (1329{\cdot}38v'' - 6{\cdot}98v''^2)$$

for transitions between states with vibrational quantum numbers $v'$, $v''$. By analysis of the rotational structure, interatomic distances of 1·487 and 1·542 A. were found for the ground and excited states, respectively.[54] A linear Birge–Sponer extrapolation gives 7·8[54] or 7·9[55] e.v. for the dissociation energy from the ground state to atoms in the ground state.[55] From a measurement of the equilibrium of phosphorus, nitrogen and phosphorus nitride at a single temperature,[51] and from a knowledge of the thermodynamic functions of the homonuclear molecules, the dissociation energy of PN has been found[51] to be 7·1 ± 0·05 e.v. (163·7 kcal./mole), a value which supersedes both the higher values quoted above, and the lower values (6·0 ± 0·8 e.v.) recommended by Gaydon[56] on the basis of the negative curvature of the Birge–Sponer plot. Its heat of formation, calculated from the new value for the dissociation energy, is $\Delta H_f^\circ(\text{PN, g}) = +24{\cdot}4$ kcal./mole; $\Delta H_f^\circ(\text{P, g})$ is taken to be 75·18 kcal./g. atom[57] and

$\Delta H_f^\circ$(N, g) to be 112·9 kcal./g. atom.[58] For the reaction $P_2(g)+N_2(g) \rightarrow 2PN(g)$, $\Delta H = 15{\cdot}0$ kcal., the value for $\Delta H_f^\circ$($P_2$, g) being taken from reference 57. Earlier calculations[59] of the thermodynamic functions of PN have been corrected for the change in dissociation energy, the equilibrium constant for the formation reaction above ranging[61] from 0·01 at 900° to 0·2 at 2000°, now agreeing qualitatively with earlier experimental results.[60]

The spectroscopic similarity of PN and the isoelectronic molecule CS has been stressed by Jevons[61–2]; its stretching constant, corrected for anharmonicity, is[63] 10·1 md./A. Empirical equations connecting internuclear distance and potential energy have been applied to PN (among other diatomic molecules), by several authors.[64–6]

Solid phosphorus nitride is also formed by the action of heat on triphosphorus pentanitride[67–9] (see below), in the reaction between active nitrogen and phosphine,[70] and, in an impure form, in the reaction between triphosphonitrilic chloride $(PNCl_2)_3$ and sodium and between phosphorus trichloride and ammonia.[71–2] It is one of the final products of decomposition[73] of phosphonitrilic oxide PNO. It may be prepared from phosphorus trichloride and ammonia[74] at −78°. Possible manufacturing processes include the thermal[75–6] and electrothermal[77] methods, and the reaction of a phosphorus halide with metallic nitrides,[78] but none of these is used in practice.

The dissociation pressure of phosphorus nitride appears not to have been measured. The solid is in equilibrium[60] with the spectroscopically detectable diatomic species at 450°, and can be sublimed[71] slowly at 500°, rapidly[51] at 900°. The yellow form is converted[67, 69] into an orange-red modification at 700° to 800°. Its heat of formation, recalculated[57] from the data of Wetroff,[79] is $\Delta H_f^\circ(\text{PN, amorp.}) = -16{\cdot}8$ kcal./mole. Its heat of depolymerization is therefore $\Delta H_{\text{depolym.}} = 41{\cdot}2$ kcal./mole, corresponding to an average P–N bond energy term of 68·3 kcal.

Phosphorus nitride is hydrolyzed when heated with water for 3 days at 215°, with formation of ammonium phosphite, ammonium phosphate and hydrogen.[80–1] It dissolves in sulphuric acid with the formation of phosphoric acid, ammonium sulphate and sulphur dioxide[69]; it is easily oxidized by sodium peroxide and by sodium nitrate.[71] It is chlorinated at 500° to trimeric phosphonitrilic chloride containing some phosphorus pentachloride,[82–3] and reacts with either atomic nitrogen[84] or ammonia[52] to give triphosphorus pentanitride (see below).

### TRIPHOSPHORUS PENTANITRIDE

Triphosphorus pentanitride is formed[85] on heating diamidotetrachloro triphosphonitrile, $P_3N_3Cl_4(NH_2)_2$, at 800° to 825°. Most of the reactions in which it is produced depend on the de-ammonation of phospham $PN_2H$ (q.v.) at temperatures[67, 69] in the range 400°–700°C. Phospham itself may be prepared by the de-ammonation of the ammonolysis products of phosphorus pentachloride[67–8, 86] or tri-[67] or tetra-phosphonitrilic chloride.[87] Triphosphorus pentanitride can be synthesized from the elements[88] by the action of a silent electric discharge in the presence of such catalysts as nickel oxide or platinum asbestos. Although normally amorphous, it can be obtained crystalline by heating in a current of ammonia[69] at 800°; the following interplanar spacings have been obtained from the *X*-ray powder pattern[52] (Table I). The conversion of PN to $P_3N_5$ is accompanied by an expansion.

Triphosphorus pentanitride is a white solid, insoluble in water,[69] but slowly hydrolyzed by hot sulphuric acid[88] or by water[88] at 180° to ammonium phosphate.[88, 81, 80] It is less stable than phosphorus mononitride to sulphuric acid,[50] but is insoluble in dilute nitric or hydrochloric acid or alkalis.[88] It decomposes in nitrogen or *in vacuo*[67, 69, 88] above 720° to phosphorus mononitride, itself unstable at this temperature, and is oxidized by air to phosphorus pentoxide.[88] Like phosphorus mononitride, it is chlorinated (at 700°) to triphosphonitrilic chloride,[89] and fluorinated to a mixture of trimeric and tetrameric phosphonitrilic fluorides.[90] Triphosphorus pentanitride reacts explosively with magnesium at the m.p. of the latter. In the reaction trimagnesium diphosphide $Mg_3P_2$ and magnesium phosphonitril-

*Table I.—Interplanar Spacings of Triphosphorus Pentanitride* ($CuK\alpha$ *Radiation*)[52]

| *d* (A.) | Intensity | *d* (A.) | Intensity | *d* (A.) | Intensity |
|---|---|---|---|---|---|
| 4·56 | S | 2·02 | MW | 1·34 | W |
| 4·20 | M | 1·83 | VW | 1·29 | W |
| 3·60 | VS | 1·71 | W | 1·21 | W |
| 2·72 | MW | 1·61 | W | 1·20 | W |
| 2·55 | VW | 1·53 | M | 1·17 | VW |
| 2·43 | MW | 1·50 | W | 1·12 | W |
| 2·36 | MW | 1·46 | MW | 1·08 | W |
| 2·27 | MW | 1·41 | W | 1·04 | VW |

M = medium, V = very, S = strong, W = weak.

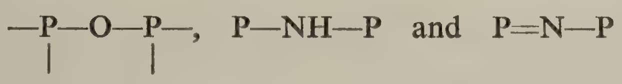
amide $PN(NMg)_2$ are formed. Calcium undergoes a similar reaction which is more violent and starts at 200°C.[115]

### TETRAPHOSPHORUS HEXANITRIDE (PHOSPHORUS PERNITRIDE)

Phosphorus trichloride reacts with ammonia to give the imide, $P_2(NH)_3$; if this is heated at 500° to 600° hydrogen is evolved rather than ammonia and a white substance of empirical composition $P_4N_6$ remains.[80, 91] More recent work, however, suggests[52] that the principal product of this reaction is $P_3N_5$. It is spontaneously inflammable in air, and is more sensitive to hydrolysis than the phosphorus mononitride into which it is converted[91] at 750°; its higher reactivity may be a consequence of the lower temperature at which it is formed. Its hydrolysis products[80–1] show that pentavalent and tervalent phosphorus atoms are present in the ratio 3:1. No evidence could be obtained from *X*-ray powder photographs[52] of a phase with $N:P=1{\cdot}5:1$. Although the existence of a compound of this formula cannot be regarded as established, the disappearance of the yellow colour of the mononitride on further nitridation shows that the product cannot be a simple mixture of the two better-known nitrides.

### PHOSPHORYL NITRIDE (PHOSPHONITRILIC OXIDE, PHOSPHORYL NITRILE)

This substance has been very little studied since its discovery by Gerhardt in 1846 (Mellor, VIII, 709). Besides the classical preparation by the thermal decomposition of phosphoramide,[138–9] the reaction of phosphonitrilic chlorides with metal oxides has also been used for its preparation.[140] The thermal decomposition of phosphoramide has been shown by infra-red studies to proceed by the elimination of ammonia and the formation of



$$-\underset{|}{P}-O-\underset{|}{P}-,\quad P-NH-P \quad \text{and} \quad P{=}N-P$$

bridges. This, together with its physical and chemical properties, shows phosphoryl nitride to be a highly polymeric substance.[138]

Phosphoryl nitride is a white powder which fuses to a black glass. A transparent form has also been described.[141] The nitride is amorphous, insoluble in the common solvents, involatile and unaffected by heating to 750°C. in air. At 1000°C. under reduced pressure it slowly decomposes to phosphorus pentoxide and polymeric phosphorus nitride. It is slowly hydrolyzed by water at 175° to ammonium dihydrogen phosphate.[139] The action of chlorine at 800°C. yields phosphorus oxychloride and a trace of phosphonitrilic chloride.[142] Phosphoryl nitride has been used as the basis of heat resistant polymers.[140]

### THIOPHOSPHORYL NITRIDE (THIOPHOSPHORYL NITRILE, PHOSPHORUS THIONITRIDE)

This compound has only been obtained by decomposing the ammonolysis products of tetra-phosphorus decasulphide (Mellor, VIII, 726). Like phosphoryl nitride it appears to be a high polymer. It is an insoluble grey-white diamagnetic solid which does not melt but decomposes with loss of nitrogen and sulphur at about 600°C. Its infra-red spectrum shows a diffuse band in the P–N stretching region (1150 cm.$^{-1}$).[143]

Thiophosphoryl nitride reacts with hydrogen at 450°C., yielding hydrogen sulphide, ammonia and phosphine. The yellowish white residue is probably a lower phosphorus hydride. The nitride reacts with chlorine at 250°C. giving phosphonitrilic chloride polymers and disulphur dichloride:

$$2(\mathrm{NPS})_n + 3n\mathrm{Cl}_2 \rightarrow 2(\mathrm{PNCl}_2)_n + n\mathrm{S}_2\mathrm{Cl}_2$$

Dry hydrogen chloride at 350°C. also breaks down the polymer:

$$(\mathrm{NPS})_n + 4n\mathrm{HCl} \rightarrow n\mathrm{NH}_4\mathrm{Cl} + n\mathrm{PSCl}_3$$

Thiophosphoryl nitride reacts with aluminium chloride at 350° to give a 1:1 adduct, $\mathrm{AlCl_3,NPS}$. This is remarkably stable, being unaffected by heating at 700°C., insoluble in the common solvents, and unaffected by water. It is cleaved by dry hydrogen chloride to give thiophosphoryl chloride and the complex $\mathrm{AlCl_3,NH_3}$.[143]

### NITRIDO-ANIONS

Compounds of lithium with phosphorus and nitrogen have been reported, such as[92] $\mathrm{Li_7PN_4}$ and[93] $\mathrm{LiPN_2}$. It is not known whether the non-metallic atoms in these compounds form simple or complex anions.

## Arsenic

*X*-Ray and thermal methods have been applied to the study of the arsenic–phosphorus system, the results being shown in Fig. 4. The phase which exists between 53% and 70% of arsenic forms dark laminæ having a graphite-like appearance and a specific resistance of between 1 and 10 ohm cm. The variation of atomic volume with composition suggests that it is structurally similar to black phosphorus or to $\beta$ or $\gamma$ arsenic.[94]

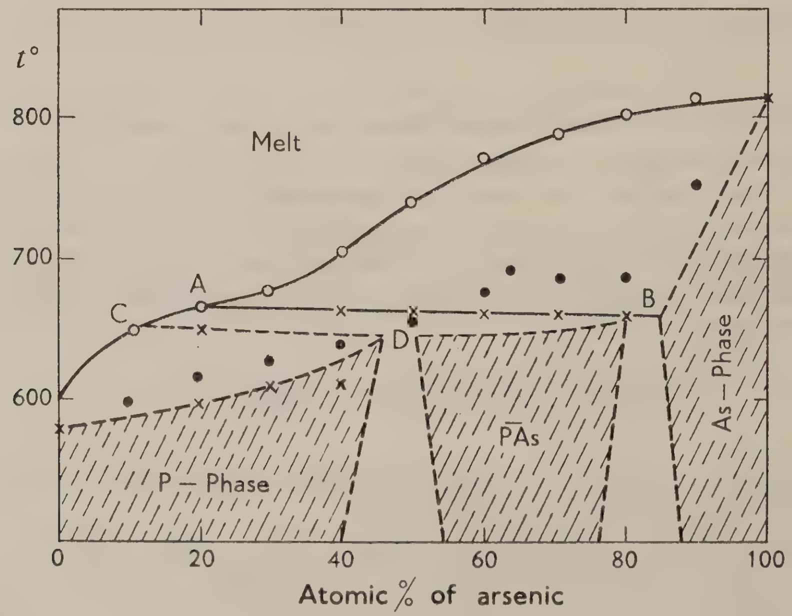


FIG. 4.—Phosphorus–arsenic phase diagram

× thermally established
○ Start of solidification
● Start of melting

Refs. p. 375

## GROUP 6

### Selenium

Compared with the phosphorus sulphides (Section XI) little is known of the corresponding selenium compounds. The structure of the blackish-violet 'pentaselenium diphosphide' made by melting red phosphorus with metallic selenium[144] has not been determined. It is amorphous, very insoluble in benzene, carbon disulphide, or carbon tetrachloride, and probably polymeric.[145] It reacts with liquid ammonia at −33° to give a mixture of $(NH_4)_2[PSe_3NH_2]$, $(NH_4)_3PSe_4$ and $(NH_4)_2[PSe_2(NH_2)NH]$ which can be separated by their differing solubilities in liquid ammonia. No monoselenophosphate has been detected.[145] Absorption spectra measurements on pentaselenium diphosphide show an absorption maximum at 2780 A.[95] Dissociation processes, as given in equations (11) and (12), are thought to account for the absorptions observed

$$\tfrac{1}{2}P_2Se_5 \rightarrow \tfrac{1}{2}P_2Se_3 + Se(^3P) \tag{11}$$

$$\tfrac{1}{2}P_2Se_5 \rightarrow \tfrac{1}{2}P_2Se_3 + Se(^1D) \tag{12}$$

Meyer[146] described a red form of triselenium tetraphosphide, m.p. 300°, which he obtained by distilling a melt of the correct composition. This form, which can also be purified by vacuum sublimation[145] is sparingly soluble in carbon disulphide. On this basis, it was suggested that the product made by heating selenium with yellow phosphorus in tetralin at 215–220°C. was a different modification.[96–7] A simple method for the preparation of this form in high purity and yield is the carbon-catalyzed reaction of yellow phosphorus with grey selenium in heptane, the product being recrystallized from tetralin.[147] 'Soluble' triselenium tetraphosphide forms fine yellow-orange crystals, m.p. 245–6°C.,[147] crystallizing in the orthorhombic system with space group *Pmnb*, $a = 9{\cdot}739$, $b = 11{\cdot}797$, $c = 26{\cdot}270$ A. The structure of the molecule is analogous to that of tetraphosphorus trisulphide (q.v.).[114] It has a density of 3·16,[96] 3·17[114] g./c.c. The infra-red and Raman spectra show strong absorptions at 360(363) and 317 $cm.^{-1}$, assigned to the symmetrical stretching frequencies of the apical P–Se and basal P–Se bonds respectively. The $^{31}P$ nuclear magnetic resonance spectrum is in accord with the structure deduced by *X*-ray methods, since it shows a doublet at +106 p.p.m. and a quartet at −38 p.p.m. (85% $H_3PO_4$).[147] The entropy of triselenium tetraphosphide at 298·15°K. is 57·26 g.-cal.deg.$^{-1}$mole$^{-1}$. It shows signs of an anomalous increase in heat capacity just above 350°K., suggesting a transformation to the plastic crystalline state similar to that occurring in tetraphosphorus trisulphide.[148] Triselenium tetraphosphide evolves phosphine and hydrogen selenide in a moist atmosphere, while with alkali it evolves phosphine, yielding a solution containing polyselenides and hypophosphite, which slowly deposits amorphous selenium.[96, 146] It burns in air,[146] and is readily oxidized by concentrated nitric acid.[96] By its reaction with liquid ammonia at −33° there results the compound $(NH_4)_2[P_4Se_3(NH_2)_2]$ which decomposes on warming. The final product is $P_4Se_3$, and no P=NH compounds can be detected as are formed in the analogous case of tetraphosphorus trisulphide[145]

$$P_4Se_3 + NH_3 \longrightarrow (NH_4)_2[P_4Se_3(NH_2)_2] \xrightarrow[-NH_3]{20^\circ} (NH_4)_2[P_4Se_3NH]$$

$$\xrightarrow[-NH_3]{90^\circ} NH_4[P_4Se_3NH_2] \xrightarrow{200^\circ} P_4Se_3 + 2NH_3$$

Patents on the use of triselenium tetraphosphide as an additive to petrol in anti-knock compositions have been granted.[98–9]

When powdered iodine is added to a solution of triselenium tetraphosphide in dry $CS_2$, a red compound $P_4Se_3I_2$ is formed. This reacts almost explosively with nitric acid and melts at 154–155°C.[111]

Substances believed to be $P_4S_2Se$ and $P_4SSe_2$[146] were prepared from the elements but m.p. measurements indicate that these are simply mixtures of $P_4Se_3$ and $P_4S_3$.[96]

Triselenium diphosphide and the compound with arsenic selenide, $As_2Se_3,P_2Se_3$, have been obtained in a vitreous state. Variations of conductivity with temperature for these glasses follow an exponential law which is usually found in crystalline semiconductors.[100]

A ternary compound, SePCu, can be obtained by direct combination of elements. Heating is carried out in a sealed tube for 2 to 3 days at 800°C. and then for 3–4 hr. at 1200°C.[101] The compound is cubic with $a=10{\cdot}15$ A. and $\rho=6{\cdot}40$ g./c.c. It is fairly inert towards acids; aqua regia attacks it slowly in the cold, concentrated nitric acid attacks it on prolonged boiling, and it is attacked by concentrated sulphuric acid. Decomposition takes place if it is heated under vacuum.[101]

Phase rule studies have shown that selenium and phosphorus form solid solutions.[102] The dotted curve *b* in Fig. 5 is due to Meyer[103] and as with curve *a* is thought not to have reached equilibrium.[102]

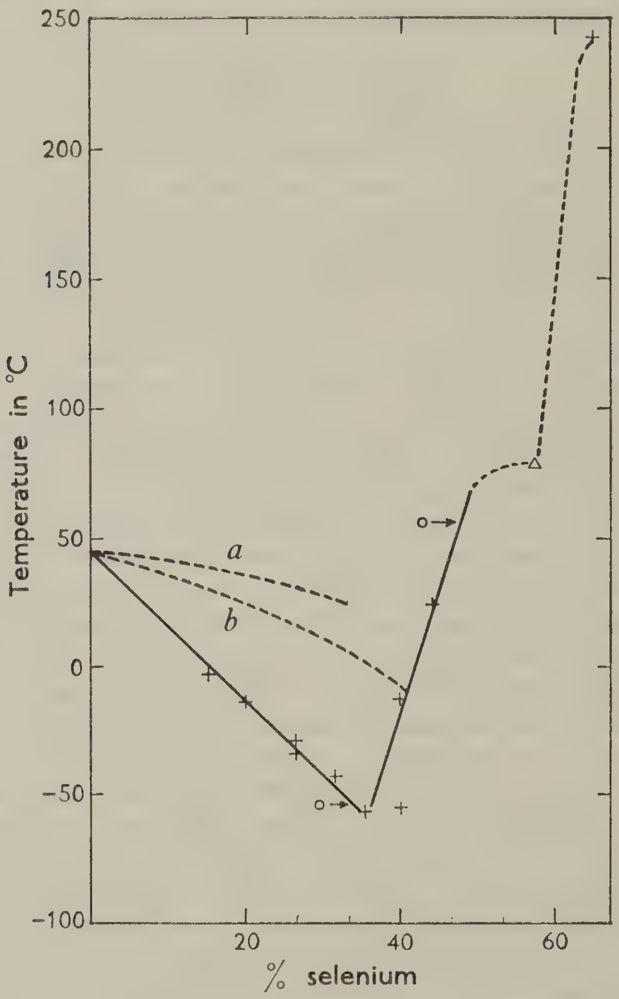


FIG. 5.—Phosphorus–selenium phase system

## Tellurium

White phosphorus and tellurium form tritellurium diphosphide $Te_3P_2$ when heated together for 1 hr. in a sealed tube at 320°C. Red phosphorus cannot be used instead of the white variety, though if red phosphorus is heated with tellurium dioxide in an open crucible at 200°C. tellurium and phosphorus pentoxide are formed which then react to give the phosphide if heated in a sealed tube at 300°C.[104] It is a black brittle compound which has a *d* 4·13 g./c.c. Chemically it is quite reactive. It is insoluble in organic solvents and water although it slowly forms phosphine in moist air. Solutions containing permanganate, dichromate, persulphate, ferric ions, mercuric ions, alkaline silver salt solutions and Fehling's solution are all reduced. Reaction of sulphur with tritellurium diphosphide produces phosphorus pentasulphide whilst tellurium dioxide is slowly formed by reaction with bromine water. If it is heated in air the phosphorus forms phosphorus pentoxide and eventually tellurium is left as a residue. Even in a sealed tube decomposition precedes melting.[104] Tritellurium diphosphide reacts with iodine in carbon disulphide solution to form tritellurium di-iodide diphosphide, $Te_3I_2P_2$. This compound is also formed when white phosphorus in carbon disulphide is allowed to react with tellurium di-iodide. The compound, which is black in colour, sublimes at 120°C. with loss of iodine; it is insoluble in water, slightly soluble in chloroform and carbon disulphide, reacts with hot 30% aqueous potassium hydroxide to form potassium telluride, is oxidized by concentrated nitric acid and decolorizes cold potassium permanganate.[104]

Tritellurium tetraphosphide has been mentioned in patents as a possible additive for lubricant and anti-knock compositions.[99, 98]

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## SECTION IX

# THE LOWER PHOSPHORUS OXIDES

BY J. E. SUCH

Only two phosphorus oxides, $P_4O_{10}$ and $P_4O_6$, have been studied extensively; some of the properties of a third, $(PO_2)_n$, have been described, but the existence of two lower oxides, $P_4O$ and $P_2O$, and one higher oxide, $P_2O_6$, is less certain.

The diatomic molecule, PO, has been observed spectrographically in the vapour state, but is unstable under ordinary conditions.[1–7, 49] Its excitation energy is 143 kcal./mole and when it dissociates, a normal oxygen and an excited phosphorus atom are produced. The dissociation energy has been reported as 6·2 e.v., a value said to be in harmony with those observed for other isoelectronic diatomic oxides, such as SO, AlO, SiO and MgO.[8] More recently a value of 6·8[50] and 5·30[51] e.v. have been reported.[50] The P–O bond length in the PO molecule is 1·447 A., and the free energy function, $-(G_T^\circ - H_0^\circ)/T$, expressed as the sum of the electronic, rotation, vibration and translation contributions, has been calculated to be[9]:

| °K. | 298 | 1000 | 1500 | 2000 | 2500 | 3000 |
|---|---|---|---|---|---|---|
| Total free energy function in entropy units | 45·23 | 55·03 | 58·51 | 61·04 | 62·98 | 64·53 |

## PHOSPHORUS TRIOXIDE, $P_4O_6$

Phosphorus trioxide, tetraphosphorus hexoxide, phosphorous oxide or phosphorous anhydride is formed when phosphorus is burnt in air or oxygen under suitable conditions. The method originally described[10] has been modified and improved[11–3] so that yields of 50–60%, based on the phosphorus burnt, have been claimed by oxidizing pure phosphorus at 46–50°C. in an atmosphere containing 75% of oxygen and 25% of nitrogen at a pressure of 90 mm. Hg and a gas flow-rate of 30 l./hr. in a 17 mm. diameter quartz tube. Phosphorus trioxide prepared in this way always contains some dissolved elementary phosphorus and can be purified by ultraviolet irradiation to convert the yellow phosphorus to the red form,[14] from which the trioxide can be separated by distillation.

Attempts to prepare phosphorus trioxide by methods other than burning phosphorus have been reported. For example, it has been claimed that phosphorus trichloride reacts with phosphorous acid to form the trioxide,[15] but this was not confirmed by later work[16–7, 20] in which the formation of an orange syrup was reported; however, 0·5% yields of the trioxide could be obtained by pyrolysis of this product.[52] Neither was any trioxide produced when the trihalide was allowed to react with acetic acid, trichloracetic acid or sodium formate.[17] The trioxide has also been reported as arising from the interaction of trimethylammonium sulphite and phosphorus trichloride in liquid sulphur dioxide,[18] and in the metathesis of phosphorus trihalides with organic metal oxides.[19] Later workers[52] have confirmed the first of these two preparations, but emphasize the difficulty of separating pure trioxide by this route.

The oxidation of yellow phosphorus by nitrous oxide at 70 mm. Hg and 550–625°C. gives good yields (30–50% on $P_4$, 70–90% on $N_2O$) of phosphorus trioxide. The product can be purified by fractional distillation under nitrogen at 30°C. and 1–3 mm. Hg.[52–3]

## Structure

### VAPOUR STATE

Evidence from vapour density[21] and electron diffraction measurements,[14, 22] indicates that the vapour of phosphorus trioxide contains $P_4O_6$ molecules, in which the phosphorus atoms are situated at the apices of a regular tetrahedron, and each of the six oxygen atoms lies on an edge equi-distant from two phosphorus atoms.

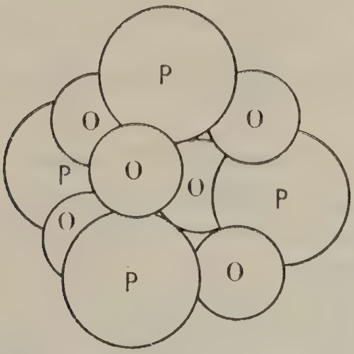

FIG. 1.—The structure of $P_4O_6$

### SOLID STATE

The Raman spectrum of solid phosphorus trioxide shows two shifts, which correspond to the strongest lines in the Raman spectrum of the liquid form, and it is therefore suggested that both contain $P_4O_6$ as a molecular species.[23–4]

### LIQUID STATE

Measurements of the freezing point depression in molten naphthalene at 80°C. show the molecular formula to be $P_4O_6$,[25] and this conclusion is supported by the Raman spectroscopic data,[23–4] which do not, however, provide sufficient evidence for a complete vibrational analysis. The $^{31}P$ nuclear magnetic resonance spectrum of the liquid exhibits, as expected, a single very narrow and intense line (chemical shift $-112{\cdot}5 \pm 0{\cdot}1$ p.p.m. from 85% $H_3PO_4$), and for this reason phosphorus trioxide has been suggested as a reference standard in $^{31}P$ nuclear magnetic resonance.[54]

## Properties

### PHYSICAL PROPERTIES

Phosphorus trioxide forms soft, colourless, monoclinic crystals which melt at 23·8°C.[26–7] and boil without change at 175·4°C. at 1 atm.[27] It is soluble in carbon disulphide,[26] from which it can be recrystallized and dissolves also in benzene, naphthalene, carbon tetrachloride, chloroform, methylene dichloride, diethyl ether, dimethyl sulphide, dioxan and tetramethyl silane.[10, 25, 38] White phosphorus is soluble in it to the extent of 1·7 g./100 g. of trioxide at 25°C.[26] The density of the solid, $d_4^{21}$, is 2·135 and of the super-cooled liquid 1·943 g./c.c.[28]

The vapour pressure of phosphorus trioxide,[27, 29] between its melting and boiling points, is given in Table I, and can be calculated for other temperatures from the equation:

$$\log_{10} p_{\text{mm.}} = 11{\cdot}0510 - 0{\cdot}0040T - 2860T^{-1}$$

in which $T$ is the absolute temperature in °K.

Refs. p. 385

*Table I.—Vapour Pressure of Phosphorus Trioxide*

| °C. | $p_{\text{mm. Hg}}$ | °C. | $p_{\text{mm. Hg}}$ |
|---|---|---|---|
| 23·8 m.p. | 1·71 | 110 | 113 |
| 25 | 1·85 | 120 | 160 |
| 50 | 8·10 | 130 | 221 |
| 60 | 13·6 | 140 | 299 |
| 70 | 22·1 | 150 | 398 |
| 80 | 34·7 | 160 | 520 |
| 90 | 52·9 | 170 | 668 |
| 100 | 78·4 | 175·4 b.p. | 760 |

The equation for the heat of vaporization[29] derived from the vapour pressure relationship is:

$$\Delta H_0 = 13{,}082 - 0{\cdot}0183T^2 \text{ g.-cal./mole } P_4O_6$$

from which the calculated heat of vaporization at the b.p. and 1 atm. is 9·4 kcal./mole $P_4O_6$, and the entropy of vaporization $P_4O_6(\text{liq.}) \rightleftharpoons P_4O_6(\text{g.})$ is $\Delta S^\circ_{448{\cdot}56} = 21{\cdot}0$ g.-cal./mole/deg. A somewhat higher value, 13·4 ± 1·0 kcal./mole $P_4O_6$, was found for the heat of vaporization at 1 atm. and the boiling point by differential thermal analysis.[46] This technique also indicated a heat of fusion of 3·0 kcal./mole $P_4O_6$, in agreement with 2·9 kcal./mole $P_4O_6$ observed by direct calorimetry.[46] These data imply a heat of sublimation of 16–17 kcal./mole $P_4O_6$ at 25°C.[47]

Heats of formation $\Delta H^\circ_f$ $P_4O_6$(c.) of $-540$ kcal./mole from white phosphorus and of $-524 \pm 8$ kcal./mole from red phosphorus were obtained by an indirect route from measurements of the heat of combustion of red phosphorus in nitric oxide, but identification of the products of combustion was not necessarily definitive.[30] More direct determinations of the heat of combustion of a well-defined sample of phosphorus trioxide give an enthalpy of formation $\Delta H^\circ_f$ $P_4O_6$(c.) of $-392$ kcal./mole.[48] In the latter experiments it was established by *X*-ray analysis, that the combustion product was substantially the hexagonal form of phosphoric oxide. Small amounts of water-insoluble residue, possibly red phosphorus, and of a compound containing trivalent phosphorus, which were also present, were thought to have arisen from the pyrolysis reaction[10]:

$$4P_4O_6 \rightarrow 3P_4O_8 + 4P_{\text{red}}$$

The thermodynamic functions $C^\circ_p$, $-(G_0 - H^\circ_0)/T$, $H_0 - H^\circ_0$, $S^\circ$ and $S_{\text{vib.}}$ for $P_4O_6$ gas at 1 atm. pressure in Table II have been calculated on the basis of the most likely available frequency assignments[45] which are also given in the same table.

The surface tension of liquid phosphorus trioxide has been given as 36·6 dynes/cm.[2] at 34·3°C. and 27·8 dynes/cm.[2] at 109·4°C., the dielectric constant 3·2 at 22°C., and the specific conductivity $1{\cdot}2 \times 10^{-7}$ at 25°C.[31]

## CHEMICAL PROPERTIES

Phosphorus trioxide is thermally stable only up to about 200°C., above which temperature the following reaction takes place[10]:

$$nP_4O_6 \rightarrow 3(PO_2)_n + nP_{\text{red}}$$

In air phosphorus trioxide ignites and burns; much study has been devoted to the mechanism of the oxidation process, especially at room temperature. Unfortunately, most of the early work appears to have been conducted with preparations contaminated with elemental phosphorus and the observations are confusing. However, Miller[26] has shown that when phosphorus trioxide is very carefully purified by recrystallization at low temperature from carbon disulphide, followed by exposure to light and volatilization, it neither glows, oxidizes in moist or dry oxygen, nor reddens when exposed to sunlight at ordinary temperatures. By addition of pure elemental white phosphorus to the pure oxide, properties previously regarded as characteristic of the trioxide, such as white opaque appearance, glowing in air and ignition on cloth, are restored. However, phosphorus trioxide apparently exerts an inhibitory effect on the glow of phosphorus itself, for it has been shown[32] that the vapour of the oxide containing phosphorus luminesces only in the presence of substances, such as ozone or moisture, sufficient in amount to destroy the trioxide completely. This inhibitory effect of phosphorus trioxide, on a molar basis, is three times as great as that of ethylene.

*Table II.—Values of* $C_p^\circ$, $-(G_0-H_0^\circ)/T$, $H_0-H_0^\circ$, $S^\circ$ *and* $S_{\text{vib.}}$ *for* $P_4O_6$ *at* 1 *atm.*

| °K. | $C_p^\circ$ g.-cal./°/mole | $-\dfrac{G_0-H_0^\circ}{T}$ g.-cal./°/mole | $H_0-H_0^\circ$ g.-cal./mole | $S^\circ$ g.-cal./°/mole | $S_{\text{vib.}}$ g.-cal./°/mole |
|---|---|---|---|---|---|
| 296·9 | 33·1 | 65·6 | 4,720 | 81·5 | 14·4 |
| 298·15 | 33·2 | 65·7 | 4,750 | 81·6 | 14·5 |
| 448·6 | 42·5 | 74·3 | 10,200 | 97·1 | 26·8 |
| 600 | 47·3 | 82·3 | 16,800 | 110·2 | 37·6 |
| 800 | 50·6 | 91·6 | 26,200 | 124·3 | 49·4 |
| 1000 | 52·3 | 99·7 | 36,100 | 135·8 | 59·2 |
| 1200 | 53·3 | 106·9 | 46,300 | 145·5 | 67·4 |
| 1400 | 53·9 | 113·3 | 56,600 | 153·7 | 74·4 |
| 1500 | 54·1 | 116·0 | 61,700 | 157·1 | 77·2 |

Frequency assignments used to calculate the above thermodynamic functions

| cm.$^{-1}$ | 613 | 400 ± 50 | 1029 | 465 | 850 ± 150 | 450 ± 100 | 919 | 643 | 407 | 302 |
|---|---|---|---|---|---|---|---|---|---|---|
| degeneracy | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 |

When dry, ozonized oxygen is passed over phosphorus-free trioxide at 25°C., the reaction products include phosphorus tetroxide and phosphoric oxide.[33] Oxygen as well as ozone participates in this reaction, which from the experimental evidence may be written:

$$8P_4O_6+4O_3+5O_2 = 5P_4O_8+3P_4O_{10}$$

When phosphorus trioxide saturated with white phosphorus is oxidized in oxygen at 25°C. in the presence of a little water vapour, about 5 moles of the trioxide per mole of phosphorus are oxidized.[33] From this and other information, it appears that phosphorus trioxide is formed as an intermediate product in the oxidation of phosphorus by dry oxygen. However, as the inhibitory action of the trioxide on the glow of phosphorus is not observed, it has also been concluded that any trioxide formed is immediately oxidized further by active oxygen (or ozone) formed in the reaction at the same time, with the result that the final low-temperature oxidation product is a mixture of the tetroxide and the pentoxide. A detailed reaction mechanism has been proposed for the oxidation of phosphorus via the trioxide to the pentoxide.[55]

If a finely-divided suspension of phosphorus in carbon tetrachloride solution is oxidized by the passage of dry air,[34] a voluminous precipitate forms which has the empirical composition $P_2O_3$; as it possesses none of the normal properties of the trioxide $P_4O_6$, for example does not melt but decomposes when heated to above 100°C. *in vacuo*, it has been suggested[35] that this reported modification might be a sheet polymer, similar to the orthorhombic forms of phosphoric oxide (q.v.). Polymeric forms of the trioxide are also possibly formed in the reaction between phosphorus and sulphur trioxide in carbon disulphide solution.[36]

With cold water phosphorus trioxide behaves as the anhydride of phosphorous acid, and when shaken rapidly with excess of water forms this acid exclusively.[37–8] Without shaking, two liquid layers are formed, which are said to react to give phosphoric acid, possibly other lower oxides and perhaps phosphine. In hot water the reaction is violent and disproportionation occurs giving rise to hydrogen phosphides, sub-oxides of phosphorus, phosphoric acid and a red product of unknown nature.

Careful addition of water to phosphorous oxide in the proportions $3H_2O:P_2O_3$ to $2H_2O:P_2O_3$ yields a mixture of phosphorous and pyrophosphorous acids. The addition of less than two moles of water per mole of phosphorous trioxide, or the careful reaction of the oxide with phosphorous or pyrophosphorous acids, gives viscous liquid mixtures. The nuclear magnetic resonance spectra of these give evidence for the presence of unstable polyphosphorous acids, $H_2(P_nH_nO_{2n+1})$. They decompose by auto-oxidation–reduction reactions, giving orthophosphoric acid and a yellow solid containing P(III).

The reaction of liquid phosphorus trioxide with dimethylformamide, dimethyl sulphoxide, dimethyl sulphite, methanol or arsenic fluoride is very violent and often accompanied by charring. However, the reaction of the oxide at room temperature with trimethyl phosphite, phosphorous tris-dimethylamide, acetic anhydride, or at elevated temperatures with phosphorus trichloride or methyltrichlorosilane can be smooth and rapid. No unique products can be isolated from these reactions which probably involve exchange, simultaneous oxidation and reduction, and in some cases rearrangements of the Michaelis–Arbuzov type (see Section XXXII).

The yellow or white solids which often result from the reactions of phosphorus trioxide are claimed to be complex network polymers containing varying proportions of P–P and P–O–P linkages, and end-stopped with terminal groups depending on the original reactants.[38]

Phosphorus trioxide is insoluble in liquid sulphur dioxide below $-60$°C., but dissolves readily at higher temperatures. The solution reacts with tetramethylammonium sulphite, $[(CH_3)_4N]_2SO_3$, to form a pale yellow compound thought to be either $[(CH_3)_4N]PO_2,SO_2$ or $[(CH_3)_4N]PO,SO_3$, which dissolves in water with the separation of sulphur.[18]

Phosphorus trioxide has been shown to act as a donor compound. So far only a few cases are clearly established, but many more are obviously possible. Thus the trioxide reacts with excess nickel tetracarbonyl displacing carbon monoxide[56]:

$$P_4O_6 + xNi(CO)_4 \rightarrow P_4O_6.(Ni(CO)_3)_x + xCO \qquad (x = 1\text{–}4)$$

$P_4O_6(Ni(CO)_3)_4$ has been isolated as a crystalline solid.[57] When the phosphorus trioxide is in excess the species $(P_4O_6)_2Ni(CO)_2$ and $(P_4O_6)_3NiCO$ can be detected, while if the reagents are present in roughly equivalent amounts polymeric structures are formed in which nickel atoms and $P_4O_6$ molecules are connected together in a three dimensional network. The nuclear magnetic resonance spectra of these adducts accord with the above formulations. Iron carbonyls appear to undergo similar reactions.[56]

Similarly $P_4O_6$ reacts with diborane giving adducts of the formulæ $P_4O_6,nBH_3$ ($n = 1$–3).[58] $P_4O_6,2BH_3$ is a white, crystalline, very hygroscopic solid, which inflames on treatment with small quantities of water. The nuclear magnetic resonance spectrum is in accord with a structure $BH_3,P_4O_6,BH_3$, formed by symmetrical cleavage of $B_2H_6$.[59] $P_4O_6,3BH_3$, isolated as well-formed crystals from chloroform, rapidly decomposes at room temperature to an equilibrium mixture of 64% $P_4O_6,2BH_3$ and 36% $P_4O_6,3BH_3$. The borane adducts react with nickel tetracarbonyl, first by substitution on the unco-ordinated phosphorus atoms, and then by displacement of $BH_3$ groups, to yield $P_4O_6[Ni(CO)_3]_4$ as the final product.[58]

Phosphorus trioxide also reacts with boron trifluoride etherate to give ether, phosphorus trifluoride and diphosphorus oxytetrafluoride, $PF_2OPF_2$ (see Section XIII). There are also indications of complexes of unknown structure with other Group III halides.[58]

## PHOSPHORUS P(III/V) OXIDES

Phosphorus trioxide dissociates on heating in a sealed tube at 200–400°C., forming a red involatile residue and a sublimate of large colourless, transparent, very hygroscopic, cubic crystals. Various workers[39] had shown that these had an empirical formula close to $PO_2$, and a measurement of vapour density[40] gave values of molecular weight ranging from 293 to 721, i.e. $n = 5$–12 in the empirical formula $(PO_2)_n$. The structure of this so-called 'diphosphorus tetroxide' has now been clarified by a study of its hydrolysis products,[60] and by *X*-ray crystal structure determinations.[61–2] It has been shown to contain at least two mixed P(III/V) oxides of different composition and crystal structures and unique *X*-ray patterns. These are a rhombohedral $\alpha$ form with the variable composition $P_4O_{8\cdot1}$–$P_4O_{9\cdot2}$, and a monoclinic $\beta$ form ($P_4O_{8\cdot0}$–$P_4O_{7\cdot7}$).[60]

$\alpha$ P(III/V) oxide forms a series of mixed crystals of the two molecules $P_4O_9$ and $P_4O_8$. The space group is $R\bar{3}c$ with unit-cell dimensions $a = 10{\cdot}05$ A. and $\alpha = 57{\cdot}0°$. The four P atoms of the molecule are located at the corners of a trigonal pyramid and linked by six oxygen atoms at the edges. The remaining two or three O atoms are terminal (apical) oxygen atoms with respect to P.[61] The density falls regularly from a maximum of 2·658 g./c.c. at $P_4O_9$ to 2·518 g./c.c. at $P_4O_{8\cdot1}$ but the lattice constants do not vary in the same regular manner. The hydrolysis products are those which would be expected from the formula, i.e. predominantly salts of phosphorous, trimeta- and triphosphoric acids from $P_4O_9$ compositions, and pyrophosphorous ($P^3$–O–$P^3$) and diphosphoric ($P^5$–O–$P^5$) acids from $P_4O_8$ compositions.

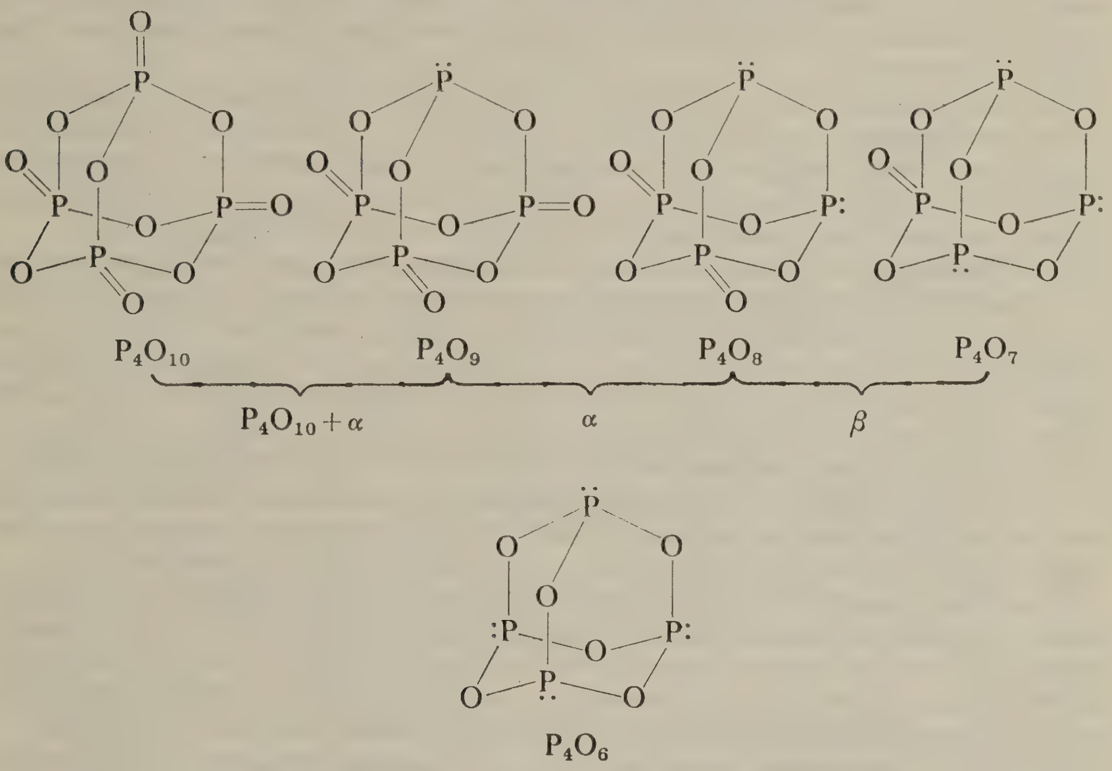

FIG. 2.—Relation of the phosphorus oxides

Similarly, $\beta$ P(III/V) oxides are mixed crystals of the two molecules $P_4O_8$ and $P_4O_7$. The composition range is narrower ($P_4O_{8\cdot0}$–$P_4O_{7\cdot7}$), products of lower oxygen content being thermally unstable. The $\beta$-oxide lattice is monoclinic with $a = 9{\cdot}66$, $b = 10{\cdot}10$, $c = 6{\cdot}93$ A. and $\beta = 96{\cdot}8°$. The $P_4O_7$ molecule has a structure similar to that of $P_4O_8$, but with one less apical oxygen atom.[62] The $\beta$-oxide on hydrolysis yields pyrophosphite, ortho- and diphosphate but no trimetaphosphate.

To summarize therefore, these P(III/V) oxides appear to be composed of varying proportions of $P_4O_7$, $P_4O_8$ and $P_4O_9$ molecules, which can, like $P_4O_{10}$, be supposed to result from the successive insertion of oxygen atoms at the four apical phosphorus positions[22] of the $P_4O_6$ molecule (Fig. 2).

None of these intermediate molecular species has yet been isolated in a pure state and free from the others. $P_4O_7$ and $P_4O_8$ molecules together form the β-oxide, $P_4O_8$ and $P_4O_9$ molecules the α-oxide. $P_4O_{10}$ and $P_4O_9$ do not form mixed crystals, and compositions in this range show the joint diffraction patterns of $P_4O_{10}$ and α P(III/V) oxide. Besides arising from the pyrolysis of phosphorus trioxide, the P(III/V) oxides are also formed by the reaction of phosphorus pentoxide with red phosphorus. Products in the α-oxide region are made at high temperatures, or using small proportions of phosphorus. The β-oxide results from the further reduction of α-oxide with phosphorus, the products being separated by fractional sublimation.[60]

## OTHER LOWER OXIDES OF PHOSPHORUS

Two oxides have been reported with the empirical formulæ $P_4O$ and $P_2O$,[41] but the evidence available is insufficient to show that they are not mixtures of phosphorus, solid phosphorus hydrides and oxyacids of phosphorus. However, it has been pointed out[35] that early workers had assigned formulations such as $P_4HO$, $P_4H_2O$, $P_5H_3O$ and $P_5H_3O_2$ to these and similar materials. A sample of $P_4O$ studied by *X*-ray diffraction showed a greater ordering of phosphorus atoms than red phosphorus, but a similar structure.[63]

The large number of red to yellow products reported in the literature (see reference 35 for bibliography), some of which, in addition to a substantial proportion of phosphorus, contain oxygen and hydrogen, are probably mixtures of a number of bodies with complex structures containing P–P, P–H, P–O and P–OH bonds. Most of them are insoluble in water, alcohol and ether, but can be burned in air.

It has been reported[42] that an orange-yellow substance is formed when phosphorus is oxidized with air in an atmosphere of water; it has an average composition phosphorus 89·0%, oxygen 10%, and hydrogen 0·8%, which corresponds to an empirical formula of $P_4OH$. Its insolubility in all common solvents and chemical behaviour suggest that it consists of a polymeric network of phosphorus atoms to which–OH groups are attached, i.e. $(P_4OH)_n$. On heating this substance in an inert atmosphere to 250–300°C., a little phosphine and products similar to red phosphorus are formed; in a normal atmosphere, the compound oxidizes to a mixture of phosphoric, phosphorous and hypophosphorous acids. Phosphine and hydrogen are evolved when the yellow substance is treated with cold normal sodium hydroxide solution.

It has been suggested[42] that the body described above, Schenck's scarlet phosphorus, so-called solid phosphine and other similar yellow materials are all the same compound. The available evidence favours attachment of OH groups to the phosphorus atoms, rather than the presence of separate P–O and P–H bonds; it is possible to neutralize the compound and obtain the sodium derivative, $(P_4ONa)_n$.

A polymeric phosphorus monoxide, $(PO)_n$, of unknown structure, has also been described. It can be prepared by two methods; in the first[43] by the electrolysis of anhydrous phosphorus oxychloride at 0°C. in the presence of triethylamine hydrochloride to increase the conductivity. Chlorine is evolved at the anode and a solid brown substance, with the empirical formula $(PO)_n$, separates at the cathode according to the equations:

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$$
$$3nPOCl_2^+ \rightleftharpoons (PO)_n + 2nPOCl_3$$

The polymeric monoxide is insoluble but stable in water, and generates phosphine in alkaline solutions. Its structure and molecular weight are not known. In the second method[44] it is formed in the reaction between anhydrous phosphorus oxybromide, $POBr_3$, and magnesium in absolute ether at the boiling point:

$$2nPOBr_3 + 3n\,Mg = 2(PO)_n + 3nMgBr_2$$

The product, although similar in composition, differs slightly in properties from that obtained by the previous method of preparation, being completely amorphous by *X*-ray examination and decomposing in moist air.

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## SECTION X

# PHOSPHORIC OXIDE AND HIGHER PHOSPHORUS OXIDES

BY J. E. SUCH

## PHOSPHORIC OXIDE

### Preparation

Phosphoric oxide, also known as phosphorus pentoxide, phosphoric anhydride or phosphoric acid anhydride, is obtained when phosphorus is burnt in excess of dry air or oxygen.

The formation of phosphoric oxide by reactions other than the oxidation of phosphorus has been reported but the products are probably not entirely anhydrous phosphoric oxide. For example, the action of dinitrogen trioxide, $N_2O_3$, on phosphorous acid, $H_3PO_3$ or phosphorus trichloride; the reaction between phosphorus oxychloride, $POCl_3$, and potassium chlorate, $KClO_3$; reactions occurring during the distillation of pyrophosphoryl chloride, and by heating bone-ash with charcoal in a current of chlorine[1]; also by the displacement of phosphoric oxide from anhydrous tripotassium orthophosphate, $K_3PO_4$, tetrapotassium pyrophosphate, $K_4P_2O_7$, or potassium metaphosphate (Kurrol salt) when these salts are heated with an excess of sulphur trioxide.[2] It has also been claimed that phosphoric oxide is liberated at the anode during the electrolysis of fused sodium phosphate.[3]

On the commercial scale, phosphorus is burnt in a specially designed burner in a current of air which has been dried by refrigeration or other methods. The phosphoric oxide vapour so formed passes into a cooling chamber where it condenses to the familiar white powder. When produced under proper combustion conditions, such commercial phosphoric oxide contains only traces of the lower oxides but, according to the conditions of storage, small proportions of condensed phosphoric acids may also be present, owing to absorption of moisture. Further purification may be carried out by sublimation at atmospheric pressure[1, 4] or *in vacuo*.[5] Alternatively the vapour may be condensed in a bed of fluidized phosphoric oxide, yielding a free-flowing dustless product in the form of small spheres or beads.[126]

The oxidation of phosphorus to phosphoric oxide is believed to proceed by a chain mechanism,[6] described more fully in Section V (page 241).

### Polymorphic Modifications

Several polymorphic modifications of phosphoric oxide are known, their presence and proportions in any sample depending on its thermal history. Whilst such polymorphs had been postulated to explain apparent inconsistencies in vapour pressure and other data, the nature of the modifications was not known until the system had been studied by optical and *X*-ray methods.[4, 16, 25] Correlated with published vapour pressure measurements,[7–13] this study indicated a one-component system with three triple-points and at least two liquids.

The known solid crystalline modifications of phosphoric oxide are:

#### 1. HEXAGONAL (H), VOLATILE LOW-TEMPERATURE OR METASTABLE FORM

Commercial phosphoric oxide consists mainly of this variety in the form of a soft fine white powder and it is always produced when the vapour of phosphoric oxide condenses on a cool surface. A powdery amorphous modification designated as the $\beta$-form is said to be present occasionally in commercial phosphoric oxide,[14] but has not been described elsewhere.

The rhombohedral crystals normally encountered belong to the hexagonal system and usually occur as small hexagonal plates.[4] Larger crystals, obtained by vacuum sublimation, are uniaxial positive and give, on optical resolution, the following refractive indices in sodium light:

$$n_\omega = 1{\cdot}469 \pm 0{\cdot}002$$
$$n_\varepsilon = 1{\cdot}471 \pm 0{\cdot}002$$

### 2. ORTHORHOMBIC (O) FORM

This second, metastable modification, consisting of aggregates of small orthorhombic crystals is obtained when the (H) form is heated for about 2 hr. at 400°C. in a closed system.[4] It is claimed that polymerization of the (H) form can also be conveniently carried out at atmospheric pressure, without excessive loss of vapour, by heating a mixture of one part of the (H) form with four parts of the (O) or (O′) form for a short time at 400°C.[15] Large crystals obtained by slow deposition from the vapour phase are bi-refringent, bi-axial negative, with refractive indices in sodium light as follow:

$$n_\alpha = 1{\cdot}545 \pm 0{\cdot}002$$
$$n_\beta = 1{\cdot}578 \pm 0{\cdot}002$$
$$n_\gamma = 1{\cdot}589 \pm 0{\cdot}002$$

### 3. ORTHORHOMBIC (O′) FORM

The (O′) form is thermodynamically stable and can be obtained as horny aggregates of relatively large and twinned crystals by heating the (H) form for about 24 hr. at 450°C., again in a closed system.[4] The indices of refraction in sodium light are reported as:

$$n_\omega = 1{\cdot}599$$
$$n_\varepsilon = 1{\cdot}624$$

and the crystals were first thought to belong to the tetragonal system.[4] Further examination, however, has shown them to be orthorhombic.[16]

### 4. HIGH-PRESSURE CRYSTALLINE FORM

The hexagonal crystalline variety of phosphoric oxide can be transformed under high pressure into a new modification which reverts to the original form when the pressure is relieved.[17] The transformation exhibits marked hysteresis, the extent of which diminishes as the temperature increases and it is believed that the transition should be truly reversible at about 500°C., whilst the new modification should persist as a metastable form at 1 atm. and *ca.* −80°C.

*Table I.—Transformation of* (H) *Form Phosphoric Oxide*; *Relationship between Temperature, Pressure and Volume Change at* 50% *Conversion*

| °C. | $P_f$ kg. cm.$^{-3}$ | $P_r$ kg. cm.$^{-3}$ | $\Delta_r$ cm.$^3$ |
|---|---|---|---|
| 25 | 3910 | 1240 | 0·485 |
| 150 | 4600 | 2330 | 0·507 |
| 200 | 4720 | 2740 | 0·521 |
| 250 | 5180 | 3510 | 0·536 |

The pressure required for half conversion to the new form in the forward, $P_f$, and the reverse, $P_r$, directions, and the volume change $\Delta_r$ for 13·0 g. of phosphoric anhydride, (H) form, are given in Table I.

The density of the high pressure form has been calculated to be 2·53 g. cm.$^{-3}$, but the crystal structure is not known.

### Liquid Forms

Three liquid forms of phosphoric oxide have been described:

(1) The metastable (H) form melts on rapid heating (m.p. 420°C., triple-point pressure 3600 mm. Hg) to a metastable mobile liquid with high vapour pressure, which quickly polymerizes to a glass containing crystals of the (O) form, with an accompanying fall in pressure.

(2) At about 562°C. and a triple point pressure of 437 mm. Hg, the metastable (O) form slowly melts to a viscous liquid; at a slightly higher temperature, 571°C., the fusion is more rapid and it has been suggested that the two liquid phases may be structurally different.[4]

(3) The stable (O′) form melts extremely slowly (m.p. 580 ± 5°C., triple-point pressure 555 mm. Hg); superheating of the crystals readily occurs and the liquid formed on melting is very viscous.[8–9, 121] This behaviour is said to be consistent with the reorganization of a polymeric structure during fusion.[18]

Besides the three solid modifications already mentioned, melts of phosphoric oxide have, on rapid cooling, a strong tendency to form glasses, which so far have received but little attention.

### Structure

#### 1. VAPOUR

The vapour of phosphoric oxide consists substantially of $P_4O_{10}$ molecules in the temperature range 700–1400°C. according to vapour density measurements.[19–20] That there is some association, at least below 1100°C., is shown by the fact that the observed vapour densities correspond to a molecular weight of 302, compared with the formula weight of 284.

The structure of the individual $P_4O_{10}$ molecule in the vapour state, consistent with electron diffraction measurements,[21, 122] is shown in Fig. 1.

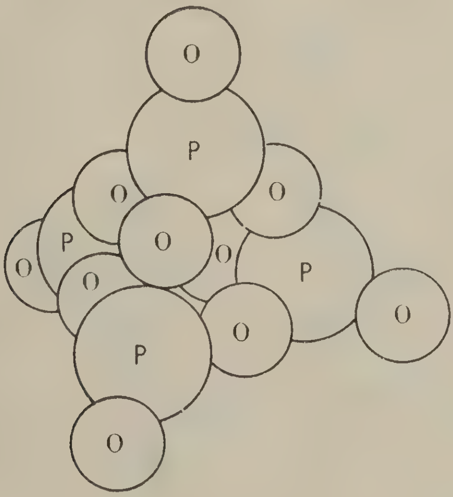


FIG. 1.—$P_4O_{10}$ molecule

The phosphorus atoms form a regular tetrahedron, and to each one is attached a closely bound oxygen atom, not otherwise connected. Each of the other six oxygen atoms is attached to two phosphorus atoms, resulting in a tetrahedral configuration of oxygen atoms around each phosphorus atom. (For bond lengths and angles see page 1160.)

## 2. SOLID FORMS

(i) The metastable solid (H) form of phosphoric oxide consists of $P_4O_{10}$ molecules with the same structure as in the vapour state, according to *X*-ray diffraction patterns,[22, 127] infra-red[128] and Raman spectra.[23–4] Since it is only the van der Waals' forces between the discrete $P_4O_{10}$ molecules of the soft crystalline (H) form which are broken during vaporization, this variety is readily volatile and also reacts violently with water.

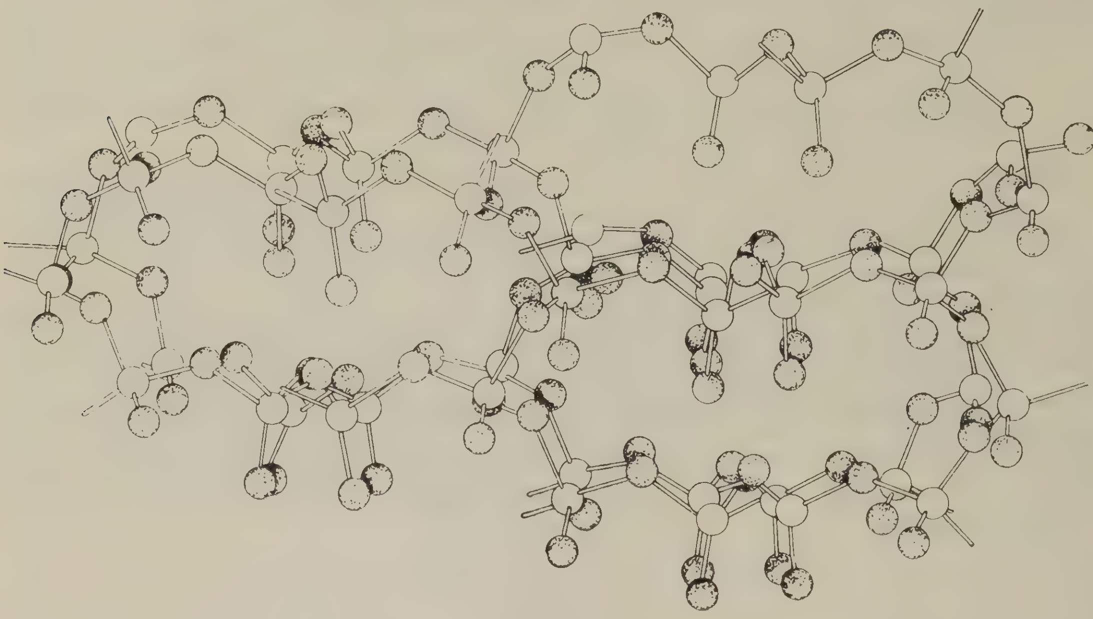


FIG. 2.—The (O) form of phosphoric oxide

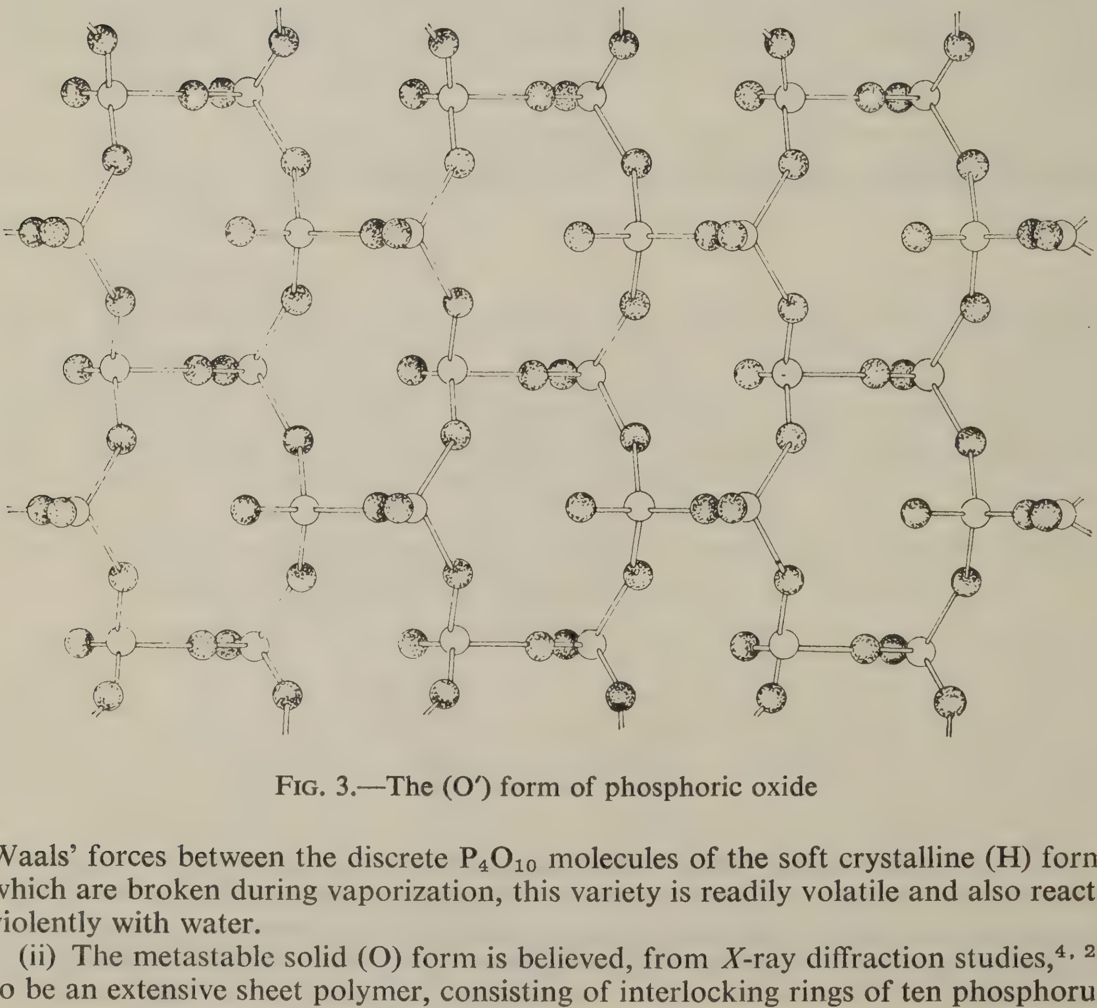


FIG. 3.—The (O′) form of phosphoric oxide

(ii) The metastable solid (O) form is believed, from *X*-ray diffraction studies,[4, 25] to be an extensive sheet polymer, consisting of interlocking rings of ten phosphorus and ten oxygen atoms; each phosphorus atom is surrounded tetrahedrally by four oxygen atoms, the atom spacings being near to those for $P_4O_{10}$ (see Fig. 2).

The crystals are hard and brittle and since covalent bonds are broken during vaporization or hydration, the solid is much less volatile and less readily attacked by water than the metastable (H) form.

(iii) The stable (O′) form is also thought to consist of an extensive corrugated sheet polymer,[16, 127] but in this modification the interlocking rings contain only four phosphorus and four oxygen atoms (see Fig. 3).

(iv) Phosphoric oxide glasses probably consist of a three-dimensional network of linked $PO_4$ tetrahedra; any discussion of their structure is usually based on the assumption that phosphoric oxide is the limiting case for phosphate glasses of the general composition $x\text{H}_2\text{O}.y\text{P}_2\text{O}_5$.[26]

(v) The structure of the liquid forms of phosphoric oxide has not been studied; it is likely that the limpid liquid obtained by heating the (H) form contains $P_4O_{10}$ molecules, which rapidly polymerize to layer or three-dimensional polymeric forms.

## Physical Properties

DENSITY (g. cm.$^{-3}$)

| | Observed | Calculated from unit cell dimensions | Calculated from refractive index |
|---|---|---|---|
| (H) form | 2·283–2·317[4] | 2·30[22] | |
| (O) form | | 2·72[25] | |
| (O′) form | 2·737–3·05[4] | | 2·89[4] |

VAPOUR PRESSURE

Vapour pressure data for the crystalline and liquid modifications of phosphoric oxide, set out in Table III and shown graphically in Fig. 4, were calculated from the

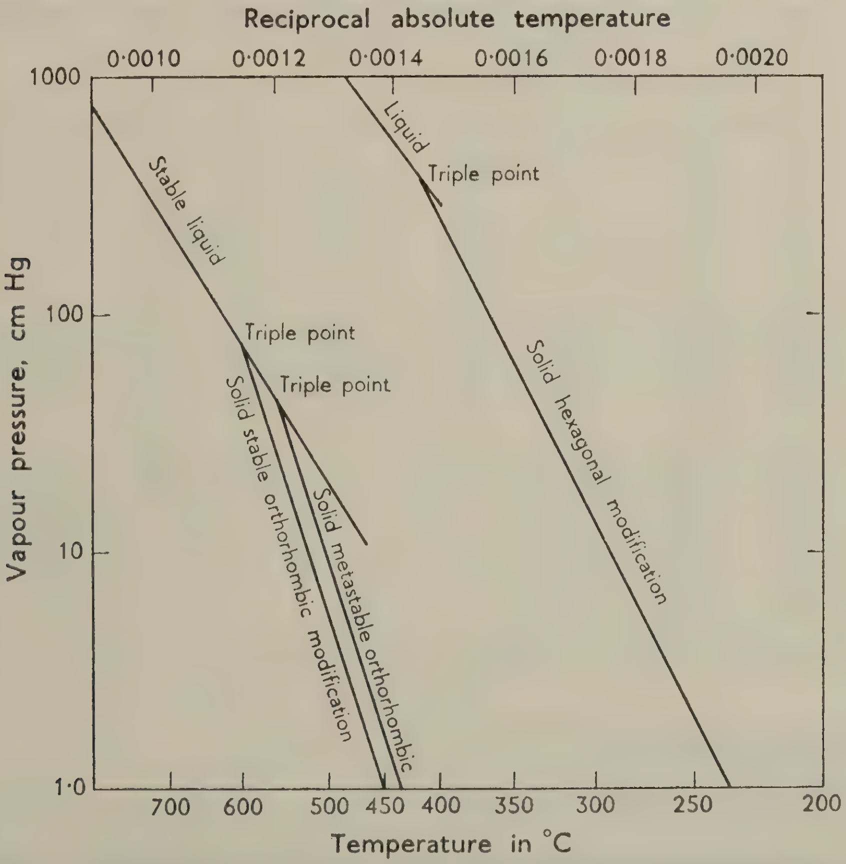


FIG. 4.—Vapour pressure of the three crystalline and two liquid forms of phosphoric oxide

equations given in Table II,[27] which in turn were derived from selected values of the triple points and heats of sublimation and vaporization of the various forms. The data were obtained from a critical survey of extensive earlier pressure–temperature relations.[4, 7, 9, 11–3]

*Table II.—Vapour Pressure Equations for Phosphoric Oxide*[27]
*($T$ = Absolute Temperature in °K.)*

| Modification | Vapour pressure equation ($p$ in cm. of mercury) | Temperature range °C. |
|---|---|---|
| Solid (H) form | $\log_{10} p = -4963/T + 9{\cdot}7163$ | 250–420 |
| Solid (O) form | ,, $= -7958/T + 11{\cdot}698$ | 440–562 |
| Solid (O′) form | ,, $= -7411{\cdot}5/T + 10{\cdot}4314$ | 480–580 |
| Liquid (H) form | ,, $= -3542/T + 7{\cdot}6663$ | 420–485 |
| Liquid (O′) form | ,, $= -4088/T + 6{\cdot}5359$ | 480–655 |

Nothing is known about the complexity of the species $(P_2O_5)_n$ which result from the depolymerizing of the crystalline modifications during conversion into the vapour, but it appears that the vapour rapidly adjusts itself to an equilibrium in which the predominant species is $P_4O_{10}$.[28]

*Table III.—Vapour Pressure of Phosphoric Oxide*[27]

| Solid (H) form | | Solid (O) form | | Solid (O′) form | | Liquid (H) form | | Liquid (O′) form | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C.) | Pressure (cm. Hg) | Temperature (°C.) | Pressure (cm. Hg) | Temperature (°C.) | Pressure (cm. Hg) | Temperature (°C.) | Pressure (cm. Hg) | Temperature (°C.) | Pressure (cm. Hg) |
| 250 | 1·7 | 440 | 1·0 | 480 | 3·9 | 420* | 360* | 490 | 15·1 |
| 260 | 2·6 | 449·3 | 1·4 | 490 | 5·2 | 425 | 392 | 500 | 17·7 |
| 270 | 3·8 | 460 | 2·1 | 500 | 7·0 | 430 | 426 | 511·5 | 21·2 |
| 280 | 5·5 | 470 | 2·9 | 509 | 9·0 | 435 | 462 | 520 | 24·1 |
| 290 | 8·0 | 483 | 4·5 | 520 | 12·2 | 440 | 501 | 530 | 27·9 |
| 300 | 11·4 | 490·1 | 5·5 | 530 | 16·0 | 445 | 542 | 533 | 29·2 |
| 310 | 16·1 | 496 | 6·7 | 540 | 20·7 | 450 | 587 | 540 | 32·2 |
| 320 | 22·3 | 498·0 | 7·1 | 547 | 24·8 | 455 | 634 | 550 | 37·1 |
| 330 | 30·8 | 500 | 7·5 | 550 | 26·8 | 458 | 664 | 562 | 43·7 |
| 340 | 41·9 | 510·3 | 10·3 | 560 | 34·3 | 460 | 684 | 570 | 48·7 |
| 350 | 56·5 | 517 | 12·5 | 566 | 39·8 | 465 | 738 | 580* | 55·5* |
| 356 | 67·3 | 520 | 13·7 | 570 | 43·8 | 470 | 795 | 586 | 59·2 |
| 360 | 75·5 | 532 | 19·3 | 575 | 49·3 | 475 | 855 | 593 | 65·5 |
| 370 | 99·9 | 540 | 24·1 | 580* | 55·5* | 480 | 919 | 600 | 71·5 |
| 380 | 131 | 546 | 28·5 | | | 485 | 987 | 613·5 | 84·2 |
| 382 | 138 | 550 | 31·7 | | | | | 620 | 91·0 |
| 390 | 171 | 556 | 37·3 | | | | | 630 | 102 |
| 400 | 221 | 557 | 38·4 | | | | | 637·5 | 111 |
| 410 | 283 | 560 | 41·5 | | | | | 650 | 128 |
| 420* | 360* | 562* | 43·7* | | | | | 656 | 137 |

* Triple points.

### THERMODYNAMIC PROPERTIES

### Heats of Vaporization, Sublimation and Fusion

The heats of vaporization, sublimation and fusion of the three modifications of phosphoric oxide, calculated from the vapour pressure equations given in Table II, are contained in Table IV.

The values in parenthesis for the (O) form are based on the assumption that the vapour pressure equation for the liquid (O′) form in Table II applies equally to the liquid phases formed from both (O) and (O′) forms. In view of the uncertainty about the nature of the transformations occurring in these liquids, the data concerning them should be regarded as only tentative.

*Table IV.—Heats of Vaporization, Sublimation and Fusion of Phosphoric Oxide*

| Modification | Latent heat of vaporization of liquid $P_4O_{10}$ kcal. mole$^{-1}$ | Latent heat of sublimation of solid $P_4O_{10}$ kcal. mole$^{-1}$ | Latent heat of fusion of solid $P_4O_{10}$ kcal. mole$^{-1}$ |
|---|---|---|---|
| (H) form $P_4O_{10}$ | 16·2 | 22·7 | 6·5 |
| (O) form $(P_2O_5)_n$ | (18·7) | 36·4 | (17·7) |
| (O′) form $(P_2O_5)_n$ | 18·7 | 33·9 | 15·2 |

A value of 17·6 kcal. mole$^{-1}$ of $P_4O_{10}$ for the heat of sublimation of the (H) form, based on calorimetric measurements, has been reported,[29] but some doubt has been expressed about the homogeneity of the sample used,[27] and the value quoted in Table IV is preferred.

## Heats of Formation, Free Energy and Entropy and Heat Capacity

After correcting the early data of Giran[30] and Thomson[31] to modern atomic weights and using revised values for the heat of combustion of naphthalene, the enthalpy of formation of crystalline (H) form phosphoric oxide has been reported to be −720 kcal. mole$^{-1}$.[32]

More accurate recent values, derived from measurements of the heat of combustion of various forms of phosphorus,[33] have been found to be:

| | $\Delta H^\circ_{f298}$ $P_4O_{10}$(H) form |
|---|---|
| From yellow phosphorus | $-713·2 \pm 1·0$ kcal. mole$^{-1}$ |
| red phosphorus (*X*-ray amorphous) | $-706·2 \pm 0·5$ ,, ,, |
| red phosphorus (form IV[34]) | $-700·7 \pm 0·4$ ,, ,, |

The free energy and entropy of phosphoric oxide ($P_4O_{10}$), considered as an ideal gas at 1 atm. pressure, have been approximately calculated over the temperature range 298–1400°K., assuming the standard entropy of this form to be 51 g.-cal.deg.$^{-1}$mole$^{-1}$ at 25°C.[35]

Using the recent value of −713·2 kcal. mole$^{-1}$ for $\Delta H^\circ_{f298}$ for the $P_4O_{10}$(H) form, the complete set of frequency assignments for the expected vibrations of the $P_4O_{10}$ molecule and the contributions to entropy from rotational and translational motion, the values for the heat content, $H_0 - E^\circ_0$, the free energy function $-(G_0 - E^\circ_0)/T$, the standard entropy $S_0$ and the heat capacity at constant pressure, $C^\circ_p$, have been re-calculated for $P_4O_{10}$ gas at 1 atm. pressure[36] and are given in Table V.

Earlier work[29] on gaseous $P_4O_{10}$ yielded a value for $C^\circ_p$ of $73·6 \pm 2·0$ g.-cal. deg.$^{-1}$ mole$^{-1}$ between 110 and 320°C.

The heat capacity of hexagonal $P_4O_{10}$ has been determined from 12 to 324°K. in an adiabatic calorimeter, and values of $C_p$, $S$, $(H - H^\circ_0)$, $(H - H^\circ_0)/T$ and $-(G - H^\circ_0)/T$ have been listed over this range. The standard entropy $S_{298·15}P_4O_{10(\text{hex})}$ is given as $54·68 \pm 0·1$ g.-cal./deg./mole, and the standard free energy of formation, $\Delta G_{298}$ as −644·8 kcal./mole.[129] The values given by these authors for the heat capacity of hexagonal $P_4O_{10}$ are lower by 2% at 100°K. and 6% at 300°K. than earlier values.[130]

*Table V.—Values of* $-\frac{G_0-E_0^\circ}{T}$, $H_0-E_0^\circ$, $S^\circ$ *and* $C_p^\circ$ *for* $P_4O_{10}$ *Gas at* 1 *atm.*

| Temperature (°K.) | Free energy function, $-\frac{G_0-E_0^\circ}{T}$ g.-cal. deg.$^{-1}$ mole$^{-1}$ | Heat content, $H_0-E_0^\circ$ g.-cal. mole$^{-1}$ | Standard entropy, $S^\circ$ g.-cal. deg.$^{-1}$ mole$^{-1}$ | Heat capacity, $C_p^\circ$ g.-cal. deg.$^{-1}$ mole$^{-1}$ |
|---|---|---|---|---|
| 298·15 | 71·9 | 6,350 | 93·2 | 43·5 |
| 400 | 79·7 | 11,100 | 107·4 | 53·1 |
| 631 | 95·7 | 24,500 | 134·5 | 64·2 |
| 900 | 111·7 | 42,500 | 159·0 | 71·7 |
| 1000 | 117·0 | 49,600 | 166·6 | 73·0 |
| 1100 | 122·5 | 57,000 | 174·3 | 74·1 |
| 1300 | 131·3 | 71,300 | 186·1 | 75·5 |
| 1500 | 139·6 | 86,100 | 197·0 | 76·4 |

Some values have also been quoted for the heats of formation and hydration of the orthorhombic (O) form of phosphoric oxide; the accuracy claimed is not high[37]

(a) $4P_{(\text{yellow})}+5O_{2(\text{gas})} = P_4O_{10(\text{orthorhombic})}$
$\Delta H^\circ_{f298} = -736{\cdot}8 \pm 14$ kcal. mole$^{-1}$

(b) $P_4O_{10(\text{orthorhombic})}+6H_2O_{(\text{liquid})} = 4H_3PO_{4(\text{solution})}$
$\Delta H^\circ_{f298} = -102{\cdot}50 \pm 0{\cdot}84$ kcal. mole$^{-1}$

Using the values for the heats of formation of the (H) form[33] and the heats of sublimation for the (H) and (O) forms respectively (Table IV), the calculated $\Delta H^\circ_{f298}$ for $P_4O_{10}$(O) form is $-727{\cdot}1$ kcal. mole$^{-1}$, a value which lies within the limits of $-736{\cdot}8 \pm 14$ kcal. mole$^{-1}$ quoted in reference 37. As part of a study of the heats of solution of crystalline and glassy phosphates, the heat of solution of sublimed phosphoric oxide (presumably the H form) in 6N HCl solution at 35°C. was found to be $-50{\cdot}15$ kcal./mole.[123]

### SURFACE TENSION

The surface tension of liquid phosphoric oxide has been measured by the pendant drop method[38]; the reported values of 60 dynes cm.$^{-1}$ at 100°C. and 50 dynes cm.$^{-1}$ at 400°C. possibly refer to highly supercooled or to partially hydrated oxide, since published melting points for all forms of phosphoric oxide are higher than the temperatures used in these determinations.

### SOLUBILITY

Phosphoric oxide (H) form is sparingly soluble in anhydrous liquid hydrogen chloride, giving a solution of low conductivity. The oxide did not react with tetramethylammonium chloride in this medium.[124]

## Chemical Properties

### THE HYDRATION OF PHOSPHORIC OXIDE

Phosphoric oxide of commerce (the low temperature, volatile (H) form) is exceedingly hygroscopic, attracting and retaining water, with which it reacts to form various oxyacids of phosphorus. For this reason it is one of the most effective drying agents, at least below 100°C.,[39] but it must be correctly distributed, e.g., on glass wool, otherwise its absorptive capacity is diminished by the formation of a crust of hydration products which have appreciable water vapour pressure. The high temperature modifications, (O) and (O′) forms, are much less effective in this respect.

Uncontrolled high temperature hydration of all varieties of phosphoric oxide with an excess of water leads, finally, to orthophosphoric acid which is almost free from other more complex phosphoric acids.

On the other hand the reactions involved and the compounds formed in controlled low temperature hydration have been the source of much speculation for many years. As early as 1884[40] marked differences were reported in the rate of solution in water of the then known forms of phosphoric oxide, and during the thirty years following the low temperature studies of Sabatier in 1888[41] much conflicting evidence emerged. It was, at that time, supposed that the reaction between phosphoric oxide and ice-cold water could be represented by:

$$n/2\ P_2O_5 + n/2\ H_2O = (HPO_3)_n$$

The value of $n$ was certainly not unity, and conductivity measurements[42] and freezing point data[43] showed it to be much greater than one.

Between 1910 and 1916 Balareff[44] studied the course of the low temperature hydration process and claimed that metaphosphoric acid was formed first and that further hydration probably proceeded *via* pyrophosphoric to orthophosphoric acid. However, as adequate analytical procedures were not then available, these observations were not conclusive.

Boratyński and his co-workers[45–8] extended earlier work[42] on the conductivities of solutions prepared by dissolving the high and low temperature forms of phosphoric oxide in ice-cold water, and concluded that the acid derived from the 'amorphous' high temperature variety was, like the oxide, strongly polymerized. This conclusion was supported by *X*-ray data on the oxides, which also indicated that the commercial product consisted substantially of the 'crystalline', or low-temperature modification. Hydration of commercial phosphoric oxide, in which the temperature was kept as low as possible in order to avoid local overheating,[45] gave a solution containing 89% of unhydrolyzed metaphosphoric acid, on the basis of a differential titration technique used by Sabatier.[41] This quantity diminished with higher initial concentrations of oxide. The observed alteration in conductivity of such solutions with time was attributed to two processes: (i) a decrease, due to formation of orthophosphate, and (ii) an increase, due to de-polymerization of the first-formed metaphosphoric acid to a simpler molecule. The former was favoured by high initial concentrations in the preparation of the solution and the latter by high temperature. With reference to the second process, the authors claimed support from Sabatier,[41] Balareff,[44] Pessel,[49] Prideaux[42] and others, and suggested that the intermediate compound of high conductivity might be the hitherto unknown monometaphosphoric acid, $HPO_3$, or the dimetaphosphoric acid, $(HPO_3)_2$, reported by Rechid[50] and Travers and Chu.[51] For the first time in this field, it was also suggested that polyphosphoric acids might be involved in the changes which metaphosphoric acid undergoes in solution.

A species believed to be dimetaphosphoric acid, $(HPO_3)_2$, was reported to have been prepared by the dehydration of orthophosphoric or pyrophosphoric acid.[50] The product was a syrupy liquid, soluble in water, which readily hydrolyzed to pyrophosphoric acid; this reaction distinguished it from other possibly more highly polymerized forms, $(HPO_3)_n$. It was also claimed that ordinary phosphoric oxide on hydration occasionally gave a solution containing a large proportion of the dimeric acid, and only in such instances was pyrophosphoric acid observed as a hydration intermediate before the final state of orthophosphoric acid was reached.

Working with phosphoric oxide freed from lower oxides by heating *in vacuo* at 70°C., Travers and Chu[51] claimed that the first hydration product of phosphoric oxide was $H_2P_2O_6$ or $(HPO_3)_2$ and that the formation of this body ought to be a normal occurrence and not to be observed only infrequently. Demonstration of the presence of the dimer was, however, claimed to be possible only if special precautions were taken to avoid local over-heating. For example, this could be done by adding the oxide in small portions either to ether saturated with water, or to pure orthophosphoric acid in dry ether, whilst agitating under slightly reduced pressure. However, evidence for the presence of dimetaphosphoric acid was not conclusive. Ideally the hydration sequence could be represented by the equations:

(1) $P_2O_5 + H_2O \rightarrow (HPO_3)_2$
(2) $(HPO_3)_2 + H_2O \rightarrow H_4P_2O_7$
(3) $H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$

and it was argued that the usual absence of pyrophosphoric acid in the progressive hydration of phosphoric oxide was explicable on the grounds that the $(HPO_3)_2$ first produced was polymerized by local heating effects and that unknown substances formed during uncontrolled hydration were derived from this hypothetical polymer. It is now believed that the dimetaphosphoric acid described could have been tetrametaphosphoric acid.[52]

Further investigations by Glixelli *et al.*[46–8] showed that solutions of the low temperature (H) form of phosphoric oxide in ice-cold water contained orthophosphoric and pyrophosphoric acids (which were estimated by independent methods). In addition, other polyphosphoric acids contributed to the differential titration of the solution between the change points of methyl orange and phenolphthalein indicators. Calculations of the heat of solution of phosphoric oxide in water[29] at 29°C., based on the assumption that orthophosphoric acid is substantially the only product of the reaction, are therefore not valid.

No clear picture of the hydration process had therefore emerged prior to the establishment of the structural arrangements of the polymorphic modifications of phosphoric oxide and to the availability of suitable procedures, such as chromatography, to analyse hydrolysates.

Possible hydration mechanisms, arising from the known molecular structures of phosphoric oxide, are believed to be as follows:

### 1. *The hydration of the hexagonal (H) form*

This polymorph exists, both in the crystalline and gaseous states in the form of individual $P_4O_{10}$ molecules, and is in fact always formed when the gas condenses on a cool surface. The molecule, idealized in Fig. 5, has four phosphorus atoms at the corners of a tetrahedron, each bonded to three oxygen atoms along the edges, with an additional oxygen atom attached to each phosphorus atom (cf. Mellor, II, Suppl. II, 1324).

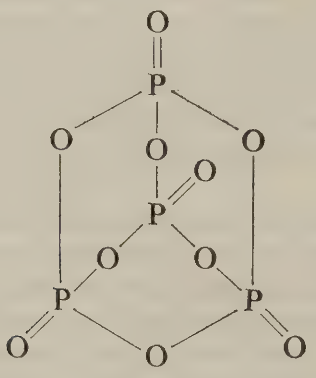


FIG. 5.—Phosphoric oxide (H) form, $P_4O_{10}$

*Stage 1.* The first stage in the hydration of phosphoric oxide (H) form can, theoretically, consist in the fission by water of any one of the six equal P–O–P bonds along the edges of the tetrahedron, with the formation of the structure shown in Fig. 6, drawn in planar configuration for the sake of clarity.

*Stage 2.* The five P–O–P bonds remaining are no longer identical in character, but assuming that the next attack by a water molecule is at the most anhydride-like—i.e. the presumably most reactive P–O–P bond, namely the oxygen bridge shown in Fig. 6—this leads directly to cyclic tetrametaphosphoric acid shown in Fig. 7.

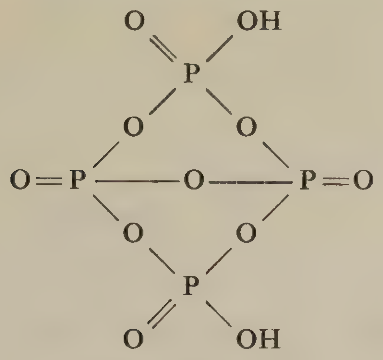


FIG. 6.—$H_2P_4O_{11}$

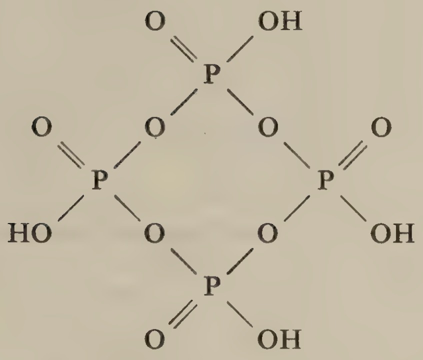
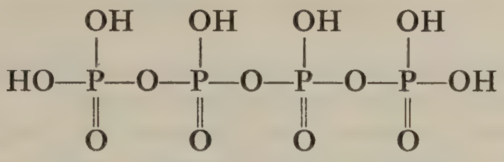


FIG. 7.—Tetrametaphosphoric acid, $H_4P_4O_{12}$ or $(HPO_3)_4$

*Stage 3.* In tetrametaphosphoric acid the P–O–P bonds are again identical in character and, irrespective of which is next attacked by water, the ring splits and tetraphosphoric acid results, as shown in Fig. 8.



$$\mathrm{HO{-}\underset{\underset{\displaystyle O}{\Vert}}{\overset{\overset{\displaystyle OH}{|}}{P}}{-}O{-}\underset{\underset{\displaystyle O}{\Vert}}{\overset{\overset{\displaystyle OH}{|}}{P}}{-}O{-}\underset{\underset{\displaystyle O}{\Vert}}{\overset{\overset{\displaystyle OH}{|}}{P}}{-}O{-}\underset{\underset{\displaystyle O}{\Vert}}{\overset{\overset{\displaystyle OH}{|}}{P}}{-}OH}$$

FIG. 8.—Tetraphosphoric acid, $H_6P_4O_{13}$

*Stage 4.* The hydration of tetraphosphoric acid could, in principle, proceed to orthophosphoric acid by the two routes, designated I and II, shown in Fig. 9.

From the available evidence[53, 60] it appears that hydration under acid conditions proceeds predominantly, and probably exclusively, by Route II, that is by attack on the end oxygen–phosphorus bridges.

Rupture of a P–O–P bond, other than that in the oxygen bridge of the molecule shown in Fig. 6, would lead to an isomeric form of tetrametaphosphoric acid, which theoretically could hydrate by three routes, designated III, IV and V, according to attack by water at any of the three types of bonds *a*, *b* (of which there are two) and *c*. These routes are shown in Fig. 10.

It is therefore apparent that, even starting with phosphoric oxide of unitary character, a hydration mechanism based on structural considerations could lead to complex mixtures of hydration products according to the conditions under which the hydration is performed. This scheme indicates the reasons which have led to confusion in the interpretation of the results obtained by many investigators in this field.

The hydration mechanism outlined above has been verified partially by the isolation in good yield (60–70%) of the sodium salt of tetrametaphosphoric acid from the hydrolysate formed by slowly adding phosphoric oxide (H) form to well stirred ice-water, first reported in 1949,[54–7] confirmed in 1950,[58] and described in greater

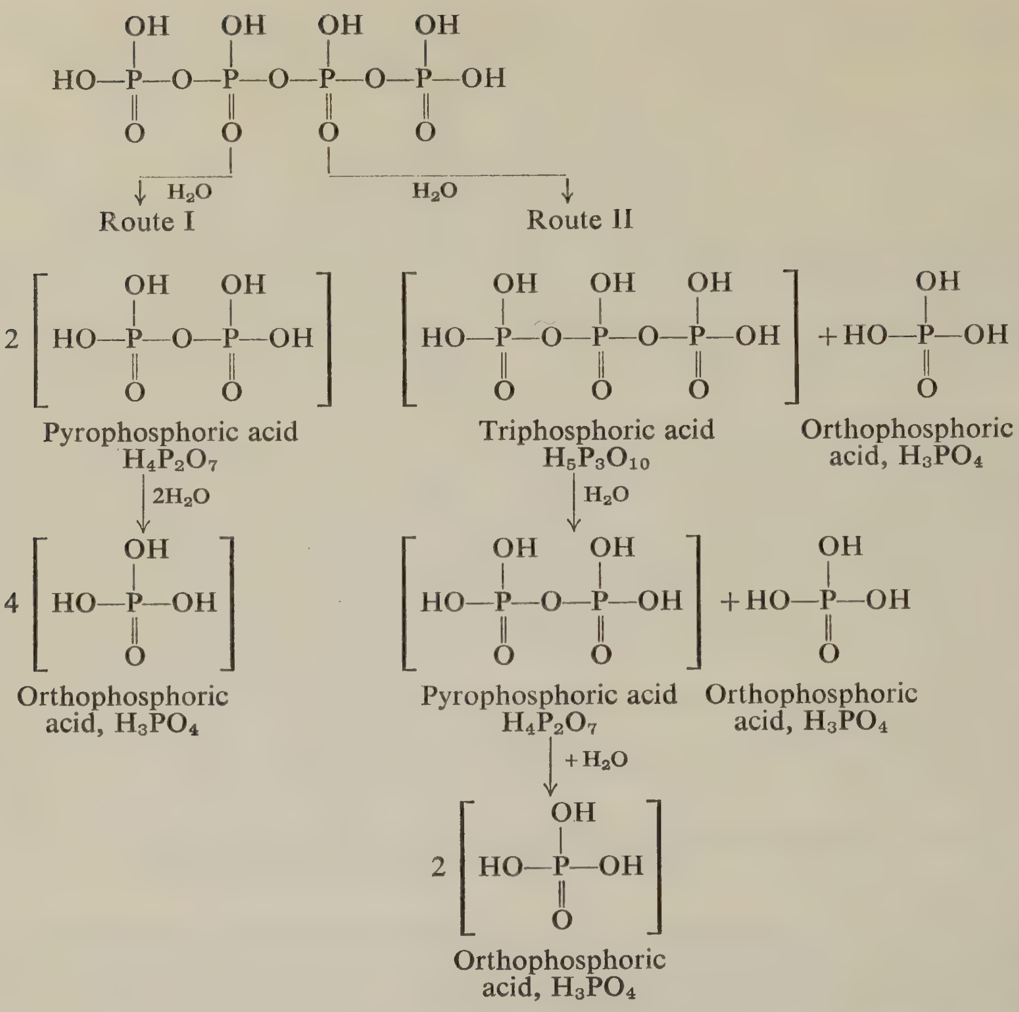

Route I
Route II
$H_2O$
Pyrophosphoric acid $H_4P_2O_7$
$2H_2O$
Orthophosphoric acid, $H_3PO_4$
Triphosphoric acid $H_5P_3O_{10}$
Pyrophosphoric acid $H_4P_2O_7$
$+H_2O$

FIG. 9.—Hydration routes for $H_6P_4O_{13}$

detail in 1952.[59] A similar study has been made on the effect of hydrolysis temperature on the yield of tetra-ammonium tetrametaphosphate.[131]

The application of paper chromatography enabled the composition of hydrolysates of the low-temperature hydration of phosphoric oxide to be determined more satisfactorily[60] and the results of one experiment at 0°C. are given in Table VI.

*Table VI.—Products of Hydration of Phosphoric Oxide (H) form in Ice-water*

| Form | Percentage of total phosphorus present |
|---|---|
| Tetrametaphosphoric acid | 77·0 |
| Tetraphosphoric (and higher polyphosphoric) acids | 3·0 |
| Trimetaphosphoric acid | 2·0 |
| Triphosphoric acid | 15·0 |
| Orthophosphoric acid | 3·0 |

Calculations[18] of the composition of the hydrolysate, based on the assumption that the scission of P–O–P linkages is completely independent of their position in the molecule, was not in accord with the experimental values quoted in Table VI; better agreement was obtained if the probability of obtaining *iso*tetrametaphosphoric acid, in Stage 2 of the hydration, was increased by a factor of about four and, in addition, if decomposition of this body at bond (*a*) to give *iso*tetraphosphoric acid, was enhanced by a factor of about 3·5.

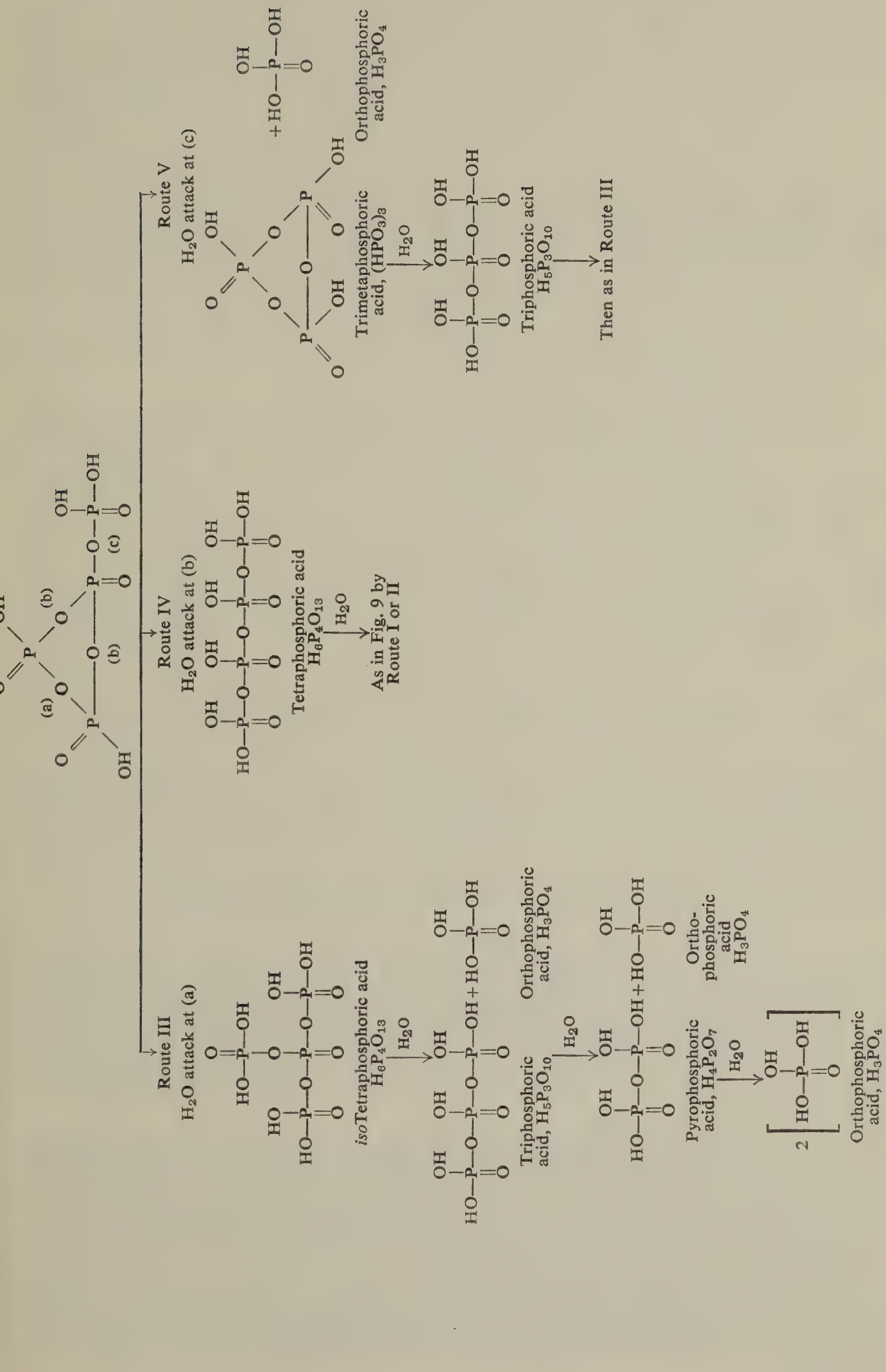

(a)
(b)
(c)
Route III
H$_2$O attack at (a)
*iso*Tetraphosphoric acid H$_6$P$_4$O$_{13}$
H$_2$O
Triphosphoric acid, H$_5$P$_3$O$_{10}$
Orthophosphoric acid, H$_3$PO$_4$
H$_2$O
Pyrophosphoric acid, H$_4$P$_2$O$_7$
Ortho-phosphoric acid H$_3$PO$_4$
H$_2$O
2
Orthophosphoric acid, H$_3$PO$_4$
Route IV
H$_2$O attack at (b)
Tetraphosphoric acid H$_6$P$_4$O$_{13}$
H$_2$O
As in Fig. 9 by Route I or II
Route V
H$_2$O attack at (c)
Trimetaphosphoric acid, (HPO$_3$)$_3$
Orthophosphoric acid, H$_3$PO$_4$
H$_2$O
Triphosphoric acid H$_5$P$_3$O$_{10}$
Then as in Route III

FIG. 10.—The hydration routes for *iso*tetrametaphosphoric acid, (HPO$_4$)$_4$

Although tetrametaphosphoric acid is the principal product of the ice-cold hydrolysis of commercial or freshly sublimed phosphoric oxide, trimetaphosphoric acid has been reported (Table VI). It has been suggested[60] that this does not arise from the hydrolysis of the hypothetical *iso*tetrametaphosphoric acid (Route IV, Fig. 10), but mainly by decomposition of a small amount (about 6%) of what are believed to be cross-linked high molecular-weight polyphosphoric acids. These appear as gelatinous flocks during the initial reaction between the oxide and water and dissolve only slowly.[60, 62] If the flocks are filtered before they decompose, then the trimetaphosphoric acid content of the hydrolysate is lower.[60] Further, if the anhydride is dissolved in boiling water, kept just alkaline, the cloudy flocks dissolve more slowly than in water alone and the solution finally contains 28% of its phosphorus content in the form of high molecular weight polyphosphoric acid species and 5% as trimetaphosphoric acid; this proportion rises to 20% on further boiling.[60] The mechanism of the reactions leading to the formation of high molecular-weight cross-linked ultraphosphates under these conditions is not completely understood, but a process similar to that advanced for the formation of linear polyphosphates with high molecular weight from those with lower degrees of polymerization is possible.[61, 63]

On the other hand, slowly dissolving gelatinous flocks are not observed when freshly sublimed phosphoric oxide is dissolved in ice-cold water, but are observed when the commercial oxide is similarly treated; this could be ascribed to the presence in the latter of modifications other than the (H) form.[4, 62]

*iso*Tetraphosphoric acid, $H_2P_4O_{11}$, and *iso*tetrametaphosphoric acid and their salts have not yet been isolated from hydrolysates obtained by the low-temperature hydration of phosphoric oxide (H) form. However, the products obtained by solvolysis with ethyl ether[64–5] and *iso*propyl ether[66] are stated to contain about 70% of the *iso*tetrametaphosphoric ester and 30% of the normal ester based on an examination of the nature and composition of their hydrolysis products. The high yield of tetrametaphosphoric acid obtained in the aqueous hydration of phosphoric oxide at low temperature has been ascribed[60] to the repulsive effect of the two ionized P–OH groups in $H_2P_4O_{11}$ (see Fig. 6) which causes the second water molecule to react with the P–O–P group of the oxygen bridge rather than with a P–O–P bonding adjacent to either of the $PO^-$ groups. In non-aqueous media the POH (or POR, $R = C_2H_5$ or $C_3H_7$) group does not tend to ionize, and there is no inductive effect to prevent the five P–O–P bonds being equally reactive. According to probability considerations, four times as much *iso*tetrametaphosphoric ester as normal ester should then be formed. Nuclear magnetic resonance data[67] have, however, been interpreted to show that only a minor proportion (3%) of the total phosphorus in the product of the reaction between ethyl ether and phosphoric oxide is present in the form of branching points[18] ($PO_4$ groups in which three oxygen atoms are shared by neighbouring $PO_4$ groups) characteristic of an *iso*tetrametaphosphoric ester.

### 2. *The hydration of the orthorhombic (O) form*

Whereas the soft crystalline (H) modification of phosphoric oxide reacts violently with water, dissolving with a hiss and usually giving off a puff of vapour or mist, the hard crystalline (O) form has a very slow rate of dissolution indeed even at steam-bath temperatures.[4, 60, 62] Dissolution proceeds by fragmentation of the crystals along cleavage cracks and often a gelatinous stage is observed, and the gel disappears but slowly on standing.

The (O) form exists in the crystalline state as an extensive array of interlocking $PO_4$ tetrahedra in a continuous structure and the theoretical consequences of the step-wise hydration of this variety have not been explored as fully as for the (H) form. However, the initial attack by water on such a sheet polymer would inevitably lead to polyphosphoric acids of high molecular weight, possibly cross-linked, which would account for the formation of gel-like bodies.

Cyclic tetrametaphosphoric acid has not been observed in the hydrolysates of this modification[60, 62]; small amounts of orthophosphoric, pyrophosphoric and trimetaphosphoric acids have been reported from chromatographic analysis, but the principal products are high molecular weight acids of which the sodium salts have an Na:P atom ratio of 0·8:1, indicating the presence of cross-linked anions.[60]

### 3. *The hydration of the (O′) form*

The rate of hydration of the (O′) modification, another sheet polymer, is also slow; with a limited amount of water it is converted into a stiff gel with the evolution of considerable heat.[4] Preferential hydration at branching or cross-linking points soon degrades the gelatinous structure, and the solution becomes more limpid. Hydrolysates are similar in composition to those reported for the (O) modification,[60] but a detailed study of the hydration process is lacking.

### ABSORPTION OF WATER VAPOUR

The three crystalline modifications of phosphoric oxide absorb water vapour from the atmosphere initially at about the same rate when samples are spread out in thin layers; eventually the rate of absorption by the (O) and (O′) forms decreases, whilst that of the (H) form continues undiminished,[4] as shown in Fig. 11.

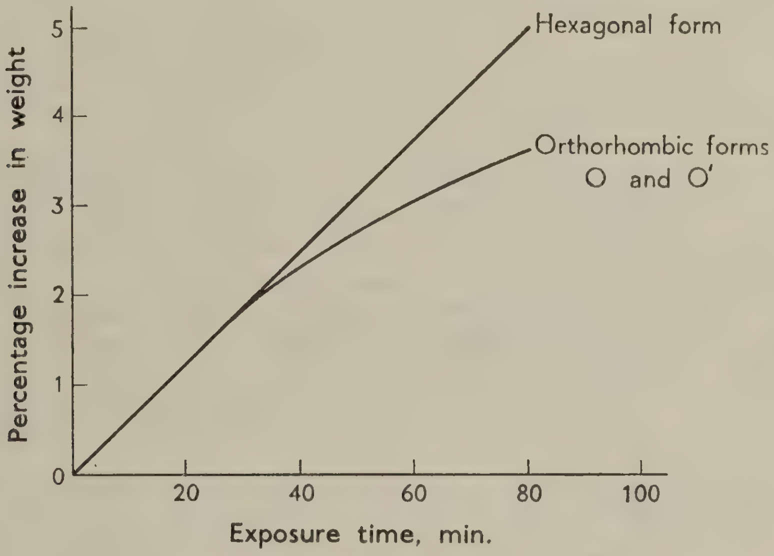


FIG. 11.—Absorption of atmospheric moisture by crystalline phosphoric oxide at room temperature

The properties and hydration characteristics of the various glassy forms of phosphoric oxide have not been reported.

Besides its avidity for free water, the (H) form of phosphoric oxide can also remove water of composition from many inorganic and organic compounds.[68] For example, it converts ethanol to ethylene and sulphuric acid to sulphur trioxide. It can also dehydrate amides to nitriles and methylarylcarbinols to the respective styrenes.[69]

Hydrogen peroxide reacts with phosphoric oxide, and these processes are described in Section XXIX.

### REACTIONS BETWEEN PHOSPHORIC OXIDE AND ORGANIC COMPOUNDS

Commercial phosphoric oxide reacts with alcohols; provided the reactions are controlled by cooling to restrict the tendency towards dehydration and the consequent formation of olefines, organic phosphates are formed, the exact composition of which depends on the proportions and moisture contents of the reagents employed.[70–2] It also combines with phosphate esters, for example triethyl phosphate,[70] and ethers,[64–6, 72] and the mechanism of the solvolysis can be regarded as being similar in many respects to that described for water.[70] The aminolysis of phosphoric oxide by various amines such as triethylamine, $(C_2H_5)_3N$, aniline, $C_6H_5NH_2$, and *p*-chloroaniline, *p*-$ClC_6H_4NH_2$, also occurs,[70, 73] the effect being the more complete the weaker is the base.[70] Phosphoric oxide also reacts with urea when the two are heated together[74] to form a non-hygroscopic water-soluble product with water-softening properties and of uncertain and possibly complex composition.

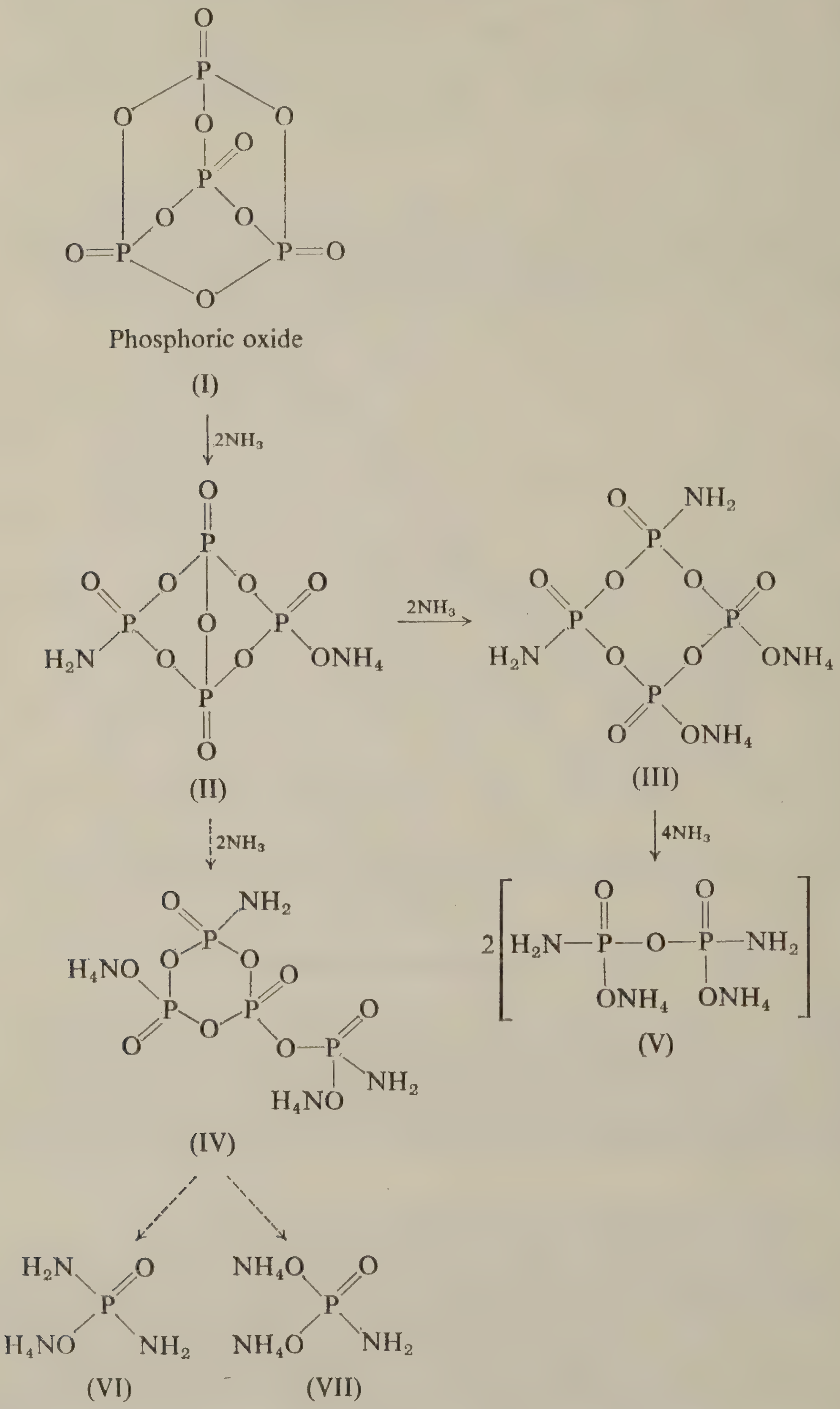


FIG. 12.—Low temperature ammonolysis of phosphoric oxide (H) form

## THE REACTION BETWEEN PHOSPHORIC OXIDE AND AMMONIA

Phosphoric oxide reacts vigorously with dry or wet ammonia to form amorphous powders,[68, 75] which are mixtures of ammonium salts of condensed phosphates containing P–$NH_2$, P–NH and P–NH–P linkages.

Incomplete reaction between very dry ammonia and purified phosphoric oxide has been claimed to be due to the encrustation of particles of the oxide by reaction products[76] and it has even been reported that no reaction occurs at all.[77] However, when the course of the reaction is followed by the changes in pressure in an ammonia-charged vessel containing resublimed phosphoric oxide, neither hypothesis is confirmed; the product has a glassy appearance.[78–9]

When gaseous or liquid ammonia is passed into phosphoric oxide, either alone or suspended in mineral oil, and the temperature kept below 150°C., further heat treatment of the solid formed is said to induce condensation or polymerization which enhances the calcium ion sequestering properties of the product. During the heat treatment, ammonia is believed to be lost by the condensation of adjacent P–$NH_2$ groups[80] and only 60–80% of the total nitrogen present is in the form of ammonium ion. If phosphoric oxide, sublimed in a current of air at 270°C., is allowed to react with ammonia gas, it is claimed that pure amidophosphoric acids are obtained[81]; these observations were verified[82] but it was not possible to propose a mechanism for the reaction on the evidence then available.

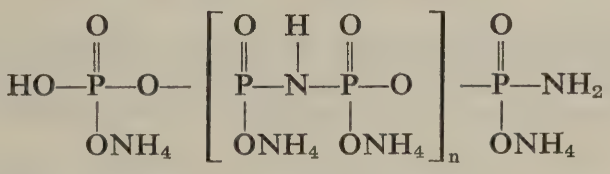
In order to avoid the difficulty of slow reactivity due to crust formation when using gaseous ammonia, the reaction between freshly sublimed phosphoric oxide and an excess of liquid ammonia has been investigated[83] by allowing the reagents to stand for a long time in sealed tubes at room temperature, or for a shorter time at 40–50°C. The products contain $P:N_{Total}:N_{Ammonium}$ in the approximate ratio 1:1·79:1·16, and paper chromatography shows the presence of several compounds. At 180–220°C. in an autoclave liquid ammonia reacts rapidly with phosphoric oxide, giving a melt. The reaction is complete at 400°C. under a pressure of 12–50 kg./cm.$^2$ The product is a colourless transparent glass, similar to those described above.[125] The course of the low-temperature ammonolysis of the (H) form of phosphoric oxide is probably similar to that already described for hydration with water, and is illustrated[83] in Fig. 12.

Since only a trace of diamidophosphate (VI) is formed under the prescribed low temperature conditions, ammonolysis is thought to proceed mainly by the route which leads to diammonium diamidodiphosphate (V), after which further ammonolysis is unlikely.[84]

At 50°C. the reaction mixture largely consists of diammonium diamidotetrametaphosphate (III) and diammonium diamidodiphosphate (V) and on further heating undergoes condensation, with loss of ammonia, to give a composition

$$P:N_{Total}:N_{Ammonium} = 1:1{\cdot}5:1$$

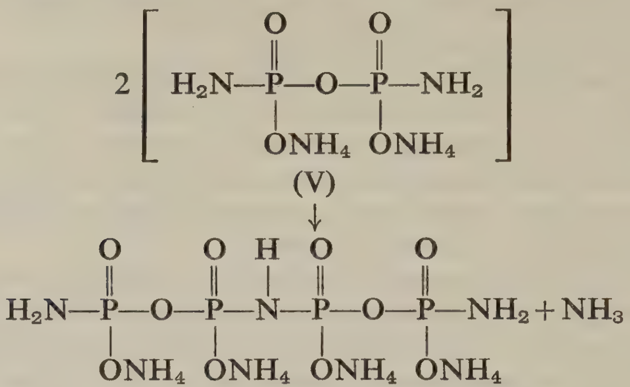
Ammonia can be lost from (V) either intra- or inter-molecularly; in the first instance it is thought[83] that the monoammonium salt of diamidophosphoric acid is first formed by loss of ammonia, and that by analogy with the behaviour of amidophosphoric acid[85] further polymerization can yield compounds of general formula:



$$HO-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-\left[\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-\overset{H}{\overset{|}{N}}-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O\right]_n-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-NH_2$$

(VIII)

When condensation occurs inter-molecularly, so that ammonia is lost from two molecules of (V), the primary product would be a derivative of an imidotetraphosphoric acid (IX), which is capable of still further condensation:



$$2\left[H_2N-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONH_4}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONH_4}{|}}{P}}-NH_2\right]$$

(V)

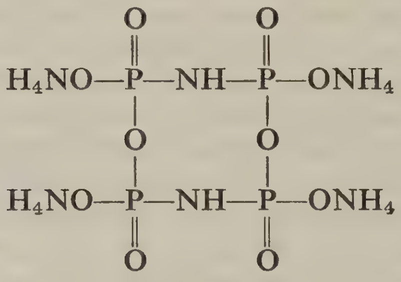
$$\downarrow$$

$$H_2N-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONH_4}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONH_4}{|}}{P}}-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONH_4}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONH_4}{|}}{P}}-NH_2+NH_3$$

(IX)

In both instances, therefore, ammonium salts of polyphosphoric acids containing P–NH–P as well as P–O–P bridges can result. From the calcium sequestering power of these condensed materials it is believed that they consist mainly of compounds of the type illustrated by formula (VIII).

In addition to linear polymers, the formation of cyclic polymers of type (X) has been suggested



(X)

when the primary reaction products of phosphoric oxide and ammonia are heated further.[80] But, so far, compounds of this class have not been isolated.

Another method for the preparation on a commercial scale of materials such as those described above, is the controlled reaction between ammonia and phosphoric oxide (produced by burning phosphorus in the same apparatus); water vapour is often introduced with the ammonia[86–9] and sometimes the initial product of a dry reaction is subsequently subjected to steam treatment to modify its properties.[90]

Similar products are also said to be formed when monoammonium dihydrogen orthophosphate is heated with ammonia and phosphoric oxide, under pressure, at 200°C. or above.[91]

### THE REACTION BETWEEN PHOSPHORIC OXIDE AND HALIDES OR OXYHALIDES

When phosphoric oxide reacts on heating with any halide, some phosphoryl halide is formed according to the equation

$$(1) \qquad 3MX+P_4O_{10} = 3MPO_3+POX_3$$

In the presence of a little water, condensation of the phosphoryl chloride, for example, to mixtures of polyphosphoryl chlorides, can occur with the formation of equivalent quantities of hydrogen chloride. When sufficient water is available the reaction may be idealized as:

$$(2) \qquad 4MX+P_4O_{10}+2H_2O = 4MPO_3+4HX$$

but it is extremely likely that the glassy solid remaining at the end of the reaction, if sodium chloride is used, consists of a mixture of polyphosphates of the type

$Na_nH_2P_nO_{3n+1}$. When phosphorus is burned with excess of oxygen in the presence of finely divided chlorides, glassy phosphates and chlorine, instead of hydrogen chloride, are produced according to the equation:

$$4MCl + P_4O_{10} + O_2 = 4MPO_3 + 2Cl_2 \tag{3}$$

The reaction expressed by equation (1) can be used for the preparation of phosphoryl chloride from sodium chloride,[92] and of phosphoryl fluoride from cryolite[92] or calcium fluoride.[93–4] The products are impure, often containing some phosphorus trihalide and/or pentahalide. For example, when a mixture of sodium chloride, calcium fluoride and phosphoric oxide is heated to 350°C. or above, a mixture of phosphorus trifluoride, $PF_3$, phosphoryl fluorides, $POF_3$, $POF_2Cl$ and $POFCl_2$, and phosphoryl chloride is formed.[95]

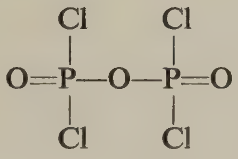
It has been claimed that the reaction represented by equation (2) can be realized in practice by burning elemental white phosphorus with air in the presence of water vapour and finely divided or volatilized alkali or alkaline earth halides[96–9]; the technical difficulties in achieving a satisfactory commercial process by this reaction are considerable.

The reaction in which chlorine is evolved, equation (3), first described in 1928,[96] has since been the subject of several other patents,[98, 100] in one of which[100] it is claimed that by spraying finely divided sodium chloride into a phosphorus flame at 2000°C., a good yield of chlorine gas can be obtained.

Phosphoric oxide also reacts with phosphorus pentahalides[101] thus:

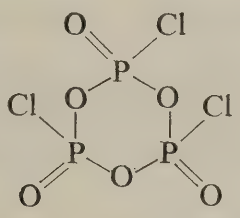
$$P_4O_{10} + 6PX_5 = 10POX_3 \tag{4}$$

and with phosphoryl chloride (in excess) in sealed tubes at 200°C. to give a viscous mixture of hygroscopic polyphosphoryl chlorides, containing chiefly pyrophosphoryl chloride, $P_2O_3Cl_4$,



$$O{=}\underset{\underset{\textstyle Cl}{|}}{\overset{\overset{\textstyle Cl}{|}}{P}}{-}O{-}\underset{\underset{\textstyle Cl}{|}}{\overset{\overset{\textstyle Cl}{|}}{P}}{=}O$$

and cyclic trimetaphosphoryl chloride, $P_3O_6Cl_3$,



with smaller amounts of linear polyphosphoryl chlorides $P_nO_{3n+1}Cl_n$ ($n = 4$–6).

Dropwise addition of fluorosulphonic acid, $HSO_3F$, to an excess of phosphoric oxide gives phosphoryl fluoride in good yield[102] according to the equation:

$$P_4O_{10} + 6HSO_3F = 2POF_3 + 2HPO_3 + 4SO_3 + 2H_2SO_4$$

The autocatalytic absorption of hydrogen chloride gas by phosphoric oxide is thought to proceed *via* intermediates such as $PO_2Cl$ or $P_2O_3Cl_4$; under extremely dry conditions the absorption is long delayed.[103]

### THE REACTION BETWEEN PHOSPHORIC OXIDE AND NITROGEN OXIDES

Phosphoric oxide does not react with nitrogen,[68] but when heated with dry dinitrogen tetroxide at 250°C. it undergoes a reaction thought[104] to be:

$$P_4O_{10} + 2N_2O_4 = P_4O_{10},4NO + 2O_2$$

or alternatively[132]:

$$N_2O_4 + 2P_4O_{10} \rightarrow (NO)_2P_8O_{21} + \tfrac{1}{2}O_2$$

The glassy white solid of unknown structure which is formed is rather less deliquescent than phosphoric oxide itself, and is also produced by the direct combination of the oxide with nitric oxide. It decomposes when treated with water to give nitric oxide and condensed phosphoric acids.[104] A similar reaction occurs at room temperature, but very much more slowly.[105] Thus the changes in properties of dinitrogen tetroxide on intensive drying with phosphoric oxide are due to chemical action and not to a shift in the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$.[105]

With dinitrogen trioxide, $N_2O_3$, at room temperature for 15 months, reaction is thought to occur according to the equation[105]:

$$P_4O_{10} + 4N_2O_3 = P_4O_{10},4NO + 2N_2O_4$$

the conversion of $N_2O_3$ to $N_2O_4$ accounting for the observed increase in vapour density.

### THE REACTION BETWEEN PHOSPHORIC OXIDE AND OXIDES, HYDROXIDES, CARBONATES AND OTHER INORGANIC SALTS

The low-temperature (H) forms of phosphoric oxide reacts with most basic and other oxides to form phosphates of various kinds. When the reaction mixture is quite dry, combination does not usually take place till heat is applied, as for example, with alumina,[62] silica,[106] boric oxide[107] or ferric oxide.[108] But if the oxides are hydrated, or if a few drops of water are added to initiate the reaction by the heat evolved during the hydration of the phosphoric oxide, then the mixtures often combine with the evolution of considerable heat and some volatilization of the phosphoric oxide.[62, 18]

Similar reactions occur with metal hydroxides, carbonates,[109–10] bicarbonates and sulphates, hydrated or otherwise, the nature of the products depending on the relative proportions of the metal to phosphorus, the amount of water available during the reaction process and the temperature attained. For example,[62] if anhydrous sodium carbonate is mixed with phosphoric oxide in the molar ratio of 2:1 and the reaction initiated by local heating, the product consists mainly of cyclic sodium trimetaphosphate, $(NaPO_3)_3$, owing to the relatively high temperature reached by the reaction mass:

$$3P_4O_{10} + 6Na_2CO_3 = 4(NaPO_3)_3 + 6CO_2$$

If, however, hydrated sodium carbonate, sodium sesquicarbonate or sodium bicarbonate is used, the reaction proceeds at a lower temperature and long chain polyphosphates in addition to orthophosphate are present in the final products; for example,

$$3P_4O_{10} + 4(NaHCO_3,Na_2CO_3,2H_2O) = 3Na_4H_2P_4O_{13} + 8CO_2 + 7H_2O$$

The reaction between phosphoric oxide and lime[92] or solid sodium hydroxide[62] is extremely violent when initiated, the product from the latter having a glassy appearance.

Calcium orthophosphate (fluoroapatite) absorbs phosphoric oxide vapour at 1000°C. to form a melt, which on chilling forms a glass consisting substantially of so-called calcium metaphosphate.[111]

### OTHER REACTIONS OF PHOSPHORIC OXIDE

#### *Phosphorus*

The reduction of phosphoric oxide by red phosphorus yields α(PIII/V) oxide with a composition in the range $P_4O_{8 \cdot 1}$ to $P_4O_{9 \cdot 2}$ (Section IX). Mixtures of phosphoric oxide and tetraphosphorus decasulphide in the appropriate proportion yield phosphorus hexaoxide tetrasulphide, $P_4O_6S_4$ (Section XII) when heated. By the evaporation of mixtures of arsenic and phosphoric acids mixed crystals of $(AsP)_2O_5$ are formed containing up to 50 mol. % of $P_2O_5$, and isostructural with $As_2O_5$.[133]

### Uses of Phosphoric Oxide

The main commercial use of phosphoric oxide is its conversion by hydration into orthophosphoric and polyphosphoric acids and in the preparation of phosphoryl chloride.

Owing to its extreme hygroscopicity it is also widely employed as a drying agent, for it is a convenient means of removing traces of moisture from vacuum systems such as those used in the production of electric light bulbs and radio valves. It is also useful for drying those gases and liquids with which it does not combine.

Phosphoric oxide is used as an intermediate in the synthesis of drugs and in the manufacture of phosphate esters of long-chain alcohols employed for uranium extraction[112] and as flotation agents.

When incorporated into air-blown asphalt[113] it stabilizes the product, both against softening at relatively high temperatures and against embrittlement at low temperatures.

## HIGHER PHOSPHORIC OXIDES

### Phosphorus Peroxide

When dry electrolytic oxygen, freed from traces of hydrogen and saturated with phosphoric oxide vapour, is passed through a heated discharge tube at low pressure, a blue-violet solid condenses in the cool section of the apparatus immediately after the discharge.[114–5] The best yields of products are said to be obtained using a silent discharge from aluminium–lead electrodes, at 3 kilovolts and 150 milliamps, at a pressure of 1 mm. Hg and a temperature of 150–220°C.

If it is assumed that phosphorus peroxide has the empirical formula $P_2O_6$,[115] then the violet compound produced under the conditions described above contains about 5% of this substance. This proportion is deduced from (*a*) determination of its oxidizing activity in liberating iodine from potassium iodide solution, or (*b*) by heating it to 130°C. (*in vacuo*), when the compound loses its colour and decomposes, liberating oxygen, the volume of which can be measured.

If phosphoric oxide vapour is passed through the heated discharge tube in the absence of oxygen, a very small amount of the violet compound is observed to condense, together with some phosphorus, or one of its lower oxides, which causes the product to inflame on exposure to the atmosphere when removed from the apparatus.[115] When cylinder argon is the carrier gas for phosphoric oxide, the condensate has the same outward appearance as when oxygen is used, but although it has a high peroxide content, based on the oxidizing activity of its solution, the latter exhibits none of the typical reactions for peroxophosphoric acids (see below). It has therefore been suggested that substances derived from the nitrogen content of the argon may be present.[115]

The violet solid is stable, if dry, and is soluble in water to give an aqueous solution which behaves like a peroxophosphoric acid. For example, the solution liberates iodine from potassium iodide, gives a yellow colour with titanyl sulphate solution and oxidizes aniline in cold hydrochloric acid solution, first to nitrosobenzene and then, after long standing, to nitrobenzene. Also, if the excess of phosphoric acid in the hydrolysate is removed by precipitation with ammoniacal magnesia mixture, the solution, when neutralized, gives with aqueous silver nitrate first a dark-coloured precipitate which rapidly turns white and then yellow.

In contrast to phosphoric oxide, the violet compound is insoluble in chloroform, so that by extraction with this solvent a product with an equivalent content of 11% $P_2O_6$ can be obtained.[115]

On the basis of the similarity of the properties of its aqueous solution with those of the peroxophosphoric acids obtained by the reaction between hydrogen peroxide and orthophosphoric or pyrophosphoric acids,[116–9] it was first suggested that the violet

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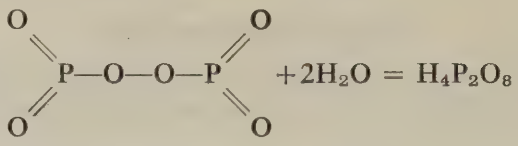
compound might be regarded as the anhydride corresponding to the acid $H_4P_2O_8$, peroxodiphosphoric acid:



Another suggestion,[120] however, is that the substance formed in the discharge tube consists of an unstable violet compound, possibly a free radical, and a colourless compound with the formula $P_4O_{11}$. The latter is thought to react with water according to the equation:

$$P_4O_{11}+4H_2O = H_4P_2O_8+H_4P_2O_7$$

to produce peroxodiphosphoric and pyrophosphoric acids, but neither peroxomonophosphoric acid nor hydrogen peroxide. The same authors have shown that if the peroxide is prepared in the presence of a little nitrogen, a nitroso compound, $P_4O_{11}.2P_4O_{10}.3NO$ is formed, which can be hydrolyzed to a nitroso tetrametaphosphate, probably $HN(PO_3)_4$.

The structure proposed[120] for $P_4O_{11}$, shown in Fig. 13, accounts for the observed hydrolysis products, assuming that all the –POP– bonds in the neighbourhood of the –POOP– group are polarized and more easily attacked by water.

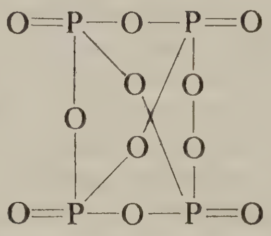


FIG. 13.—Structure of phosphorus peroxide

The anhydride corresponding to peroxomonophosphoric acid, $H_3PO_5$, which is said to exist in equilibrium with peroxodiphosphoric acid, $H_4P_2O_8$, in aqueous solution according to the equilibrium:

$$H_4P_2O_8+H_2O \rightleftharpoons H_3PO_5+H_3PO_4$$

has not been described.

The true nature and structure of oxides of phosphorus higher than phosphoric oxide therefore, await more detailed investigations by physico-chemical techniques.

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## SECTION XI

# THE PHOSPHORUS SULPHIDES

BY A. F. CHILDS

The existence of four sulphides of phosphorus has been well authenticated. Three of these, viz., tetraphosphorus trisulphide, $P_4S_3$, tetraphosphorus heptasulphide, $P_4S_7$, and tetraphosphorus decasulphide, $P_4S_{10}$, were identified by Stock (Mellor, VIII, 1048) from the melting point–composition diagram of the phosphorus–sulphur system. The fourth, tetraphosphorus pentasulphide, $P_4S_5$, first prepared by Bouloch by the interaction of $P_4S_3$ and iodine in carbon disulphide, and regarded as a solid solution both by him and Stock, has been shown[1, 3] to be a definite compound with a unique and unexpected structure. The molecular structures of these four sulphides have been determined by *X*-ray single crystal techniques[2–5] and are supported by a variety of physical and chemical data which will be discussed in detail for each sulphide individually. For comparative purposes, however, the structural data for these compounds are brought together in Tables I and II and the structures illustrated in Fig. 1. More accurate data, in general agreement with those in Fig. 1, have been reported.[115]

*Table I.—X-Ray Crystallographic Data for the Phosphorus Sulphides*

| | $P_4S_3$ | $P_4S_5$ | $P_4S_7$ | $P_4S_{10}$ |
|---|---|---|---|---|
| Crystal System | Orthorhombic | Monoclinic | Monoclinic | Triclinic |
| *a* (A.) | 10·63 | 6·41 | 8·87 | 9·07 |
| *b* (A.) | 9·69 | 10·94 | 17·35 | 9·18 |
| *c* (A.) | 13·72 | 6·69 | 6·83 | 9·19 |
| $\alpha°$ | | | | 92·4 |
| $\beta°$ | | 111·7 | 92·7 | 101·2 |
| $\gamma°$ | | | | 110·5 |
| Space group | $D_h^{16}-Pnmb$ | $P2_1$ | $P2_1/n$ | $P\bar{1}$ |
| No. of molecules | 8 | 2 | 4 | 2 |
| Observed density | 2·03 | 2·17 | 2·19 | 2·09 |
| Calculated density | 2·06 | 2·15 | 2·19 | 2·10 |
| Reference | 2 | 3 | 4 | 4 |

*Table II.—Interatomic Distances in the Phosphorus Sulphides*

| | $P_4S_3$ | $P_4S_5$ | $P_4S_7$ | $P_4S_{10}$ |
|---|---|---|---|---|
| P—S (A.) | 2·235 | 2·08–2·19 | 2·08 | $2{\cdot}08_5$ |
| P=S (A.) | — | 1·94 | 1·95 | $1{\cdot}95_5$ |
| P—P (A.) | 2·090 | 2·21 | 2·35 | — |
| Reference | 2 | 3 | 4, 5 | 4 |

It will be seen that each of these sulphides contains four phosphorus atoms arranged roughly tetrahedrally. The structures are regular and, except in the case of $P_4S_5$, the observed interatomic bond distances show little variation from the mean. There appear to be no analogies for the unusually long P–P bond distance observed in $P_4S_7$.

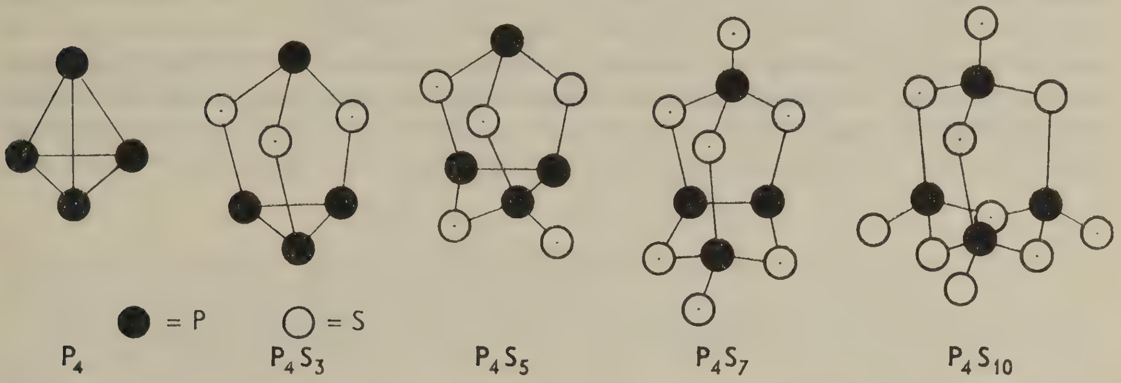


FIG. 1.—The structures of the $P_4$ molecule and of molecules of the phosphorus sulphides

The bond angles in $P_4S_{10}$ do not differ significantly from the tetrahedral values of 109° 28′, and most of the bond angles in $P_4S_7$ are also near this value. In $P_4S_3$ the P–P–P bond angles are 60°, as in $P_4$, while the P–S–P bond angles are 102°. Variation in bond angles is again at its highest in the irregular molecule $P_4S_5$.

While, therefore, there seems little doubt of the existence of these four sulphides,

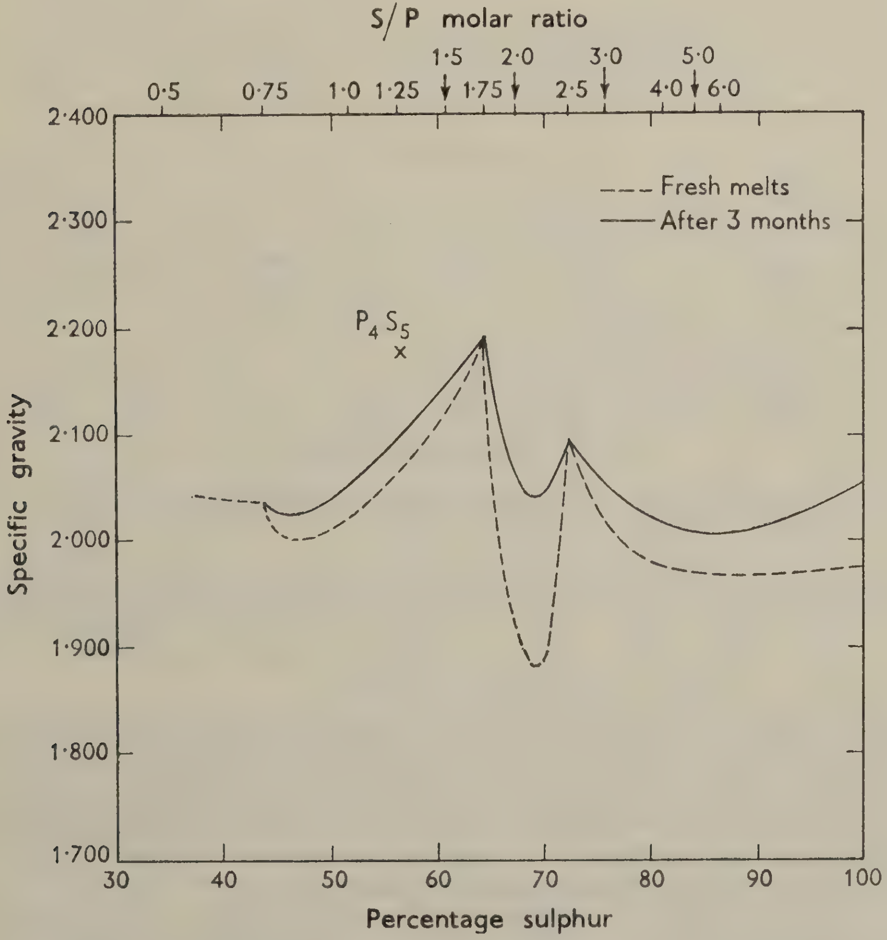


FIG. 2.—Specific gravity of phosphorus–sulphur compositions

evidence for others is more debatable. A study of the variation of density with composition in phosphorus sulphide melts[1] shows only three maxima corresponding to $P_4S_3$, $P_4S_7$ and $P_4S_{10}$, respectively (Fig. 2). On the other hand, repetition of the work of Giran (Mellor, VIII, 1049), on the melting point of red phosphorus–sulphur compositions which had been refluxed under nitrogen, shows well-defined maxima corresponding to $P_4S_3$, $P_4S_7$, $P_4S_{10}$ and $P_4S_{24}$.[6] The curve (Fig. 3) is of the same form as that of Giran, differing only in that a maximum at 308·5°, corresponding to the composition $P_4S_7$, is observed in place of Giran's maximum of 296° for $P_4S_6$. Later workers detected four maxima in the liquidus line corresponding to the percentage compositions by weight 27·9% P (=$P_4S_{10}$) m.p. 288 ± 1°C., 35·6% P (=$P_4S_7$) m.p. 308 ± 1°C., 56·3% P (=$P_4S_3$) m.p. 174 ± 1°C., and 66% P (=$P_4S_2$) m.p. 46 ± 2°C., as

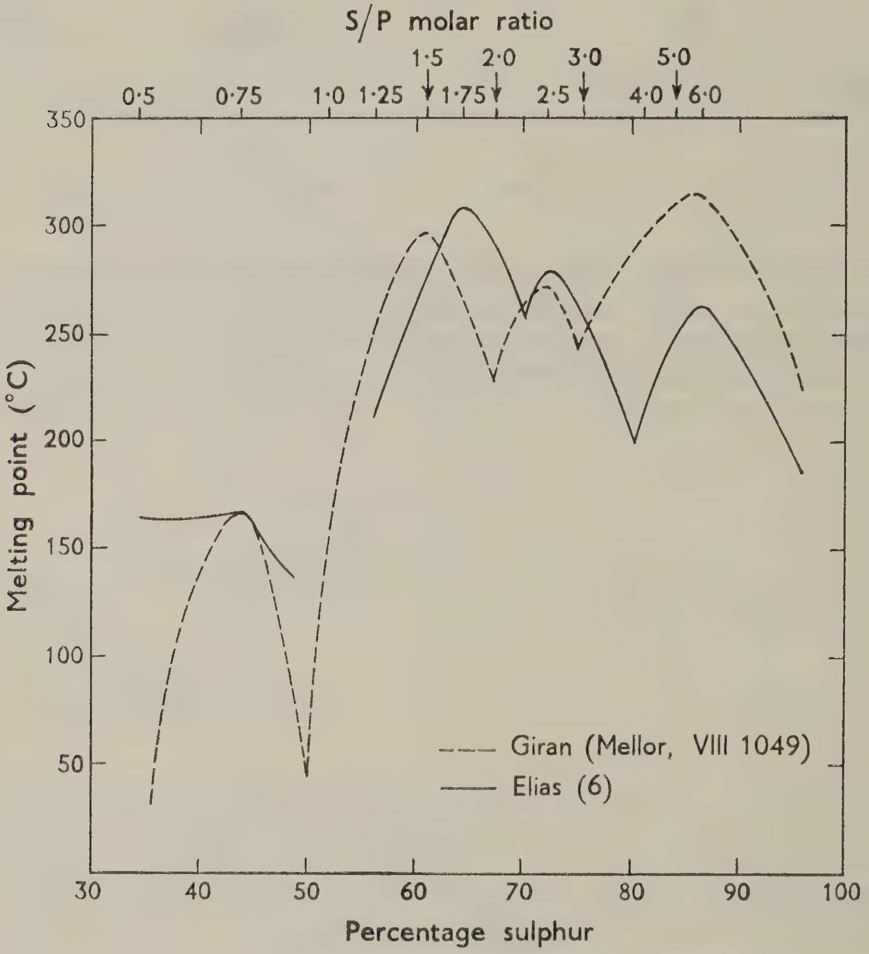


FIG. 3.—Fusion curve of phosphorus–sulphur compositions

well as the compounds $P_4S_6$ with a peritectic at 232°C. and $P_4S_5$ (peritectic 162°C.). $P_4S_{24}$ was not detected in this study. Eutectics were observed as follows: $P_4S_{10}$–S, 1·5% P, 112°C.; $P_4S_7$–$P_4S_{10}$, 31·0% P, 251°C.; $P_4S_3$–$P_4S_5$, 53·0% P, 106°C.; $P_4S_2$–$P_4S_3$, 18°C.; $P_4$–$P_4S_2$, 77 ± 2% P, −65 ± 5°C.[106]

After considerable controversy[1, 7–10] the existence of tetraphosphorus hexasulphide seemed to be established by its identification as a phase of variable composition, stable within narrow temperature limits, and having a unique *X*-ray diffraction pattern.[11] The same pattern is exhibited by the thiohydrolysis product of phosphorus trichloride. However, an *X*-ray diffraction study of this product shows it to be a defect form of tetraphosphorus heptasulphide.[108] Evidence[8, 9] for the existence of tetraphosphorus pentasulphide in this material can be explained by assuming its decomposition on dissolution in carbon disulphide. On the other hand, there seems little doubt that the sulphides $P_2S_4$ and $P_8S_{11}$, described by Dervin

(Mellor, VIII, 1047), were in reality impure $P_4S_7$ and $P_4S_5$.[8–9] Phosphorus monosulphide, $(PS)_n$, hitherto known only in the monomeric state as a spectroscopic entity,[12–3] has been prepared[14] by the action of magnesium on thiophosphoryl bromide:

$$2PSBr_3 + 3Mg \rightarrow \frac{2}{n}(PS)_n + 3MgBr_2$$

Ill-defined phosphorus sulphides are also formed by the interaction of phosphine with sulphur or hydrogen sulphide,[15] their composition depending on the initial proportions of reactants:

$$2PH_3 + nS \rightarrow 3H_2S + P_2S_{n-3}$$
$$2PH_3 + nH_2S \rightarrow (3+n)H_2 + P_2S_n$$

The former reaction goes rapidly to completion at 450°C.; the latter is slower, although more rapid than the decomposition of either reactant alone.

Nuclear magnetic resonance, viscosity and reactivity studies of a range of phosphorus sulphide melts of varying composition[78, 83] have led to the conclusion that the simple 'cage' molecules described above, and based essentially on $P_4$, predominate in melts of low sulphur content. Using S/P mole ratios greater than about 0·9, however, amorphous phosphorus sulphides of infinitely variable composition can be obtained. These, while having some 'cage' structures, contain also a considerable amount of random network polymer, the proportion and detailed structure of which depend on the S/P molar ratio. At very high S/P ratios, for example, the system can be regarded as a network of elastomeric plastic sulphur $(S\mu)_n$ cross-linked by phosphorus.[84–5] Two good reviews of this subject have appeared[78, 99] which draw on earlier work.[8, 10] Commercial aspects have also been discussed.[41]

## TETRAPHOSPHORUS TRISULPHIDE (PHOSPHORUS TETRITATRISULPHIDE; PHOSPHORUS SESQUISULPHIDE), $P_4S_3$

### Preparation

A typical plant for the commercial manufacture of this substance has been described.[16] The process involves batch reaction of molten sulphur and phosphorus at 350°C. followed by distillation of the product at 410°C. and 760 mm. Hg. Alternative continuous procedures, in which the heat of reaction is absorbed in a 'heel' of product or used to effect its distillation, have been suggested.[17–8] The introduction of small amounts of oxygen during the distillation has been claimed to improve the colour of the product[19] but this leads to the formation of oxysulphides, and an inert atmosphere is usually employed, the distillate being cast into blocks or flaked. The technical product can be purified by boiling with water for 2 hr. to hydrolyse other sulphides, drying, and dissolving in carbon disulphide. The solution is further dried over phosphorus pentoxide, filtered and evaporated. If well-formed crystals are required, the sulphide can be recrystallised by slowly cooling an almost saturated benzene solution from a temperature not exceeding 40°C., air being excluded by a blanket of inert gas.[20]

### Physical Properties

Tetraphosphorus trisulphide forms brick-shaped yellow crystals, showing full orthorhombic symmetry with right angles clearly displayed. Often the crystals are six-sided and columnar along the [*b*] axis with [100] the well-developed face. Sometimes poorly formed pyramidal faces develop at the ends.[6, 8] When warmed this solid undergoes a transition at 313·90°K.,[107] which has been detected by adiabatic calorimetry,[107] microscopy, dilatometry and differential thermal analysis.[2, 20–1] The entropy of transition $\Delta S_t$ is $7{\cdot}85 \pm 0{\cdot}03$ g.-cal./(mole °K.), and the enthalpy of transition $2{\cdot}464 \pm 0{\cdot}01$ kg.-cal./mole, in close agreement with earlier estimates of $+3{\cdot}4$[20]

and $+2{\cdot}5 \pm 0{\cdot}3$ kg.-cal./mole,[21] obtained by differential thermal analysis. The entropy of $P_4S_3$ at 298·15°K. is 48·60 g.-cal./(mole °K.).[107] Nothing is known of the crystal structure of the high temperature form, which melts at 172·6–173°C.[22] to a brownish-yellow liquid. The heat and entropy of fusion have been determined by differential thermal analysis to be $+1{\cdot}2$ kcal./mole and 2·8 e.u./mole, respectively, while the heat of vaporization is $+12{\cdot}2$ kcal./mole,[21] $+15{\cdot}2 \pm 0{\cdot}4$ kcal./mole, giving an entropy of vaporization of $22{\cdot}4 \pm 0{\cdot}7$ e.u./mole.[106] Values for the b.p. (408°C.,[23, 8] $407 \pm 2$°C.[10, 6]) agree with earlier determinations. The density of the low-temperature crystalline form, calculated from $X$-ray diffraction data (2·06 g./c.c.),[24] is also in good agreement with the earlier experimental value given by Stock (2·03 g./c.c. at 17°C.) and confirmed by later workers.[1] The apparent linear coefficients of expansion of the two forms, as determined by $X$-ray diffraction, are $2{\cdot}5 \pm 0{\cdot}6 \times 10^{-6}$°K.$^{-1}$ (295–308°K.) for the low-temperature form and $3{\cdot}2 \pm 1{\cdot}7 \times 10^{-6}$°K.$^{-1}$ (319–337°K.) for the high temperature form.[107] The density and surface tension of liquid tetraphosphorus trisulphide at 172·2°C. are 1·7935 g./c.c. and 22·86 ergs/cm.$^2$, respectively.[25]

The parachor calculated from these data accords better with the accepted structure for $P_4S_3$ (Fig. 1) than with previously proposed structures. The value of 0·81$D$ for the dipole moment of $P_4S_3$ in benzene solution, and the molar refractivity 57·8 (calc. 59·3),[26] are also in harmony with the general outlines of the structure given in Fig. 1 and Tables I and II, which has been established both by electron diffraction in the vapour phase[27–8] and $X$-ray diffraction on the solid.[2, 24, 29] The high-resolution phosphorus nuclear magnetic resonance spectrum[30–1] of $P_4S_3$ shows two absorptions, corresponding to the presence of phosphorus atoms in two distinct environments. One peak, a quadruplet of chemical shift $-71 \pm 1$ p.p.m., corresponds to a single phosphorus atom connected through sulphur atoms to three other phosphorus atoms. The other, a doublet of chemical shift $+120 \pm 1$ p.p.m., is attributed to three identical phosphorus atoms, presumably those in the $P_3$ ring. The high absolute values of the chemical shifts, as in the $P_4$ molecule, can probably be explained by the effect on bond hybridisation of the high degree of strain in the molecule. They are confirmed by independent measurements on the solid sulphide, using a rapidly rotating specimen technique, which gave values of $+103$ and $-72$ p.p.m. relative to 85% phosphoric acid.[111]

The Raman spectrum of tetraphosphorus trisulphide[22] shows absorption frequencies of 442, 420, 290 and 87 cm.$^{-1}$ (symmetrical, polarized) and 486, 384, 341, 221 and 154 cm.$^{-1}$ (degenerate, depolarized). Force constants calculated from these data on the basis of the accepted structure gave the values $f_1$ ($P_4S_1$) $16{\cdot}3 \times 10^4$, $f_2$ ($P_1S_1$) $16{\cdot}7 \times 10^4$, and $f_3$ (P–P) $10{\cdot}7 \times 10^4$ dynes/cm., respectively, in reasonable agreement with values calculated by the empirical rules of Badger and Gordy. The compound shows broad infra-red absorption maxima at 430 and 473 cm.$^{-1}$.[22] Other workers have found absorptions at 427, 440, 447 and 486 cm.$^{-1}$ in carbon disulphide solution.[6]

As would be expected in a molecule having no centre of symmetry, solid tetraphosphorus trisulphide shows no pyro- or piezoelectric effects.[20] An estimated value of 32 kcal./mole for the enthalpy of formation of tetraphosphorus trisulphide[21] was obtained by a study of the reaction:

$$4P_{\text{red}} + 3S_{\text{liq.}} \xrightarrow{200\text{–}260°} P_4S_{3\ \text{liq.}}$$

using differential thermal analysis. The observed heat of reaction was corrected for heat of fusion and phase change.

## Chemical Properties

Solutions of tetraphosphorus trisulphide in organic solvents absorb oxygen from the air, with precipitation of a yellowish-white amorphous solid having the empirical formula $P_4S_3O_4$, which is discussed in more detail on page 435.[32]

The trisulphide shows the lowest reactivity towards water of all the phosphorus sulphides, a fact which may be used in its purification. The conductivity of a suspension of the sulphide in water at 60°C. is almost zero and increases only very slowly with time, unlike $P_4S_7$ and $P_4S_{10}$ which both show a great increase in conductivity over 3 hr.[33, 99] Hydrolysis is reasonably rapid in boiling dilute sodium hydroxide solution, giving hydrogen sulphide, phosphine and varying amounts of phosphorus oxyacids (see Table III).

*Table III.—Alkaline Hydrolysis Products of Tetraphosphorus Trisulphide*

| Reference | Atoms of P per mole $P_4S_3$ determined as: | | | | |
|---|---|---|---|---|---|
| | $PH_3$ | $H_3PO_2$ | $H_3PO_3$ | $H_3PO_4$ | unaccounted for |
| 1 | 0·2 | 0·6 | 3·0 | — | 0·2 |
| 10 | 0·1 | 1·5 | 2·0 | 0·2 | 0·2 |

In acid solution hydrolysis is much slower[1] but under paper chromatographic conditions using an acid solvent, a mixture of thiophosphates, thiophosphites and thiohypophosphites is formed from $P_4S_3$, as in the case of $P_4S_7$ (q.v.)[34]; alkaline oxidative hydrolysis leads to a mixture of phosphorus oxyanions, discussed more fully under the heptasulphide.[97, 109]

The primary product of the reaction between tetraphosphorus trisulphide and liquid ammonia at −33°C. is a hygroscopic brownish-orange compound of empirical formula $P_4S_3{,}4NH_3$.[23] When heated *in vacuo* this loses ammonia in stages to give $P_4S_3{,}3NH_3$ and $P_4S_3{,}2NH_3$, both of which revert to the original compound on solution in liquid ammonia. At higher temperatures the compound $P_4S_3{,}2NH_3$ gives $P_4S_3$, ammonia and a residue which, after repeated extraction with ammonia followed each time by heating at 180°C., is found to have the formula $P_4S_2NH{,}4NH_3$. $P_4S_2NH{,}4NH_3$ is a dark brown solid, non-hygroscopic and insoluble in liquid ammonia. It evolves between one and two moles of ammonia when heated to 180°C. *in vacuo*, giving a mixture of $P_4S_2NH{,}3NH_3$ and $P_4S_2NH{,}2NH_3$.

The compounds $P_4S_3{,}nNH_3$ and $P_4S_2NH{,}4NH_3$ are soluble with hydrolysis in water or alkalis, but insoluble in dilute non-oxidizing acids. When heated at even higher temperatures (275°C.) extensive decomposition sets in and $P_4S(NH)_2$ and $P_4(NH)_3$ are formed. The latter compound is deep orange, insoluble in $CS_2$ and is decomposed by hot alkalis with evolution of phosphine. If heated to 400°C. it evolves phosphorus vapour and ammonia, phosphorus pentanitride, $P_3N_5$, being formed:

$$5P_4(NH)_3 \rightarrow 2P_3N_5 + 5NH_3 + 14P$$

This extensive series of reactions can be explained completely on the basis of the accepted structure for the trisulphide as shown in Fig. 4.

Tetraphosphorus trisulphide reacts rapidly with iodine in carbon disulphide, 7·9–8·1 atoms of iodine being taken up per mole of sulphide. Besides the phosphorus tri-iodide previously reported (Mellor, VIII, 1051), tetraphosphorus heptasulphide can be isolated in 34% yield based on the equation:

$$7P_4S_3 + 24I_2 \rightarrow 16PI_3 + 3P_4S_7$$

An intermediate compound, $P_4S_3I_8$, was postulated,[1] but the reaction has more recently been shown to proceed via the known $P_4S_3I_2$,[35] an orange yellow solid, m.p. 120·5°C. A solution of the trisulphide in carbon disulphide also rapidly takes up 8·2–8·4 atoms of bromine per mole of sulphide, but no products have been recorded. The reaction between tetraphosphorus trisulphide and bromine in an aqueous acid medium has been followed potentiometrically. The results correspond to no simple mechanism, between 23 and 28 atoms of bromine being absorbed for every mole of the trisulphide, and sulphur is the only product observed.[1]

Because of its low reactivity, tetraphosphorus trisulphide is little used as an intermediate in organic chemistry. With alcohols, a melt of composition $P_4S_4$ (which was presumably composed mainly of $P_4S_3$ [83]) gave poor yields of dialkyl phosphorothioites, $(RO)_2PSH$, and di- and trialkyl phosphorodithioates, $(RO)_2PS(SH)$ and $(RO)_2PS(SR)$.[36] Ethylmagnesium bromide gives a mixture of di- and triethylphosphine, triethylphosphine sulphide and tetraethylphosphonium bromide in poor yields. With phenylmagnesium bromide the yield of phenylated products is rather better and diphenyldithiophosphinic acid, $(Ph)_2PS(SH)$, is formed as an additional product.[37] Unlike tetraphosphorus decasulphide the trisulphide does not react with anisole.[38]

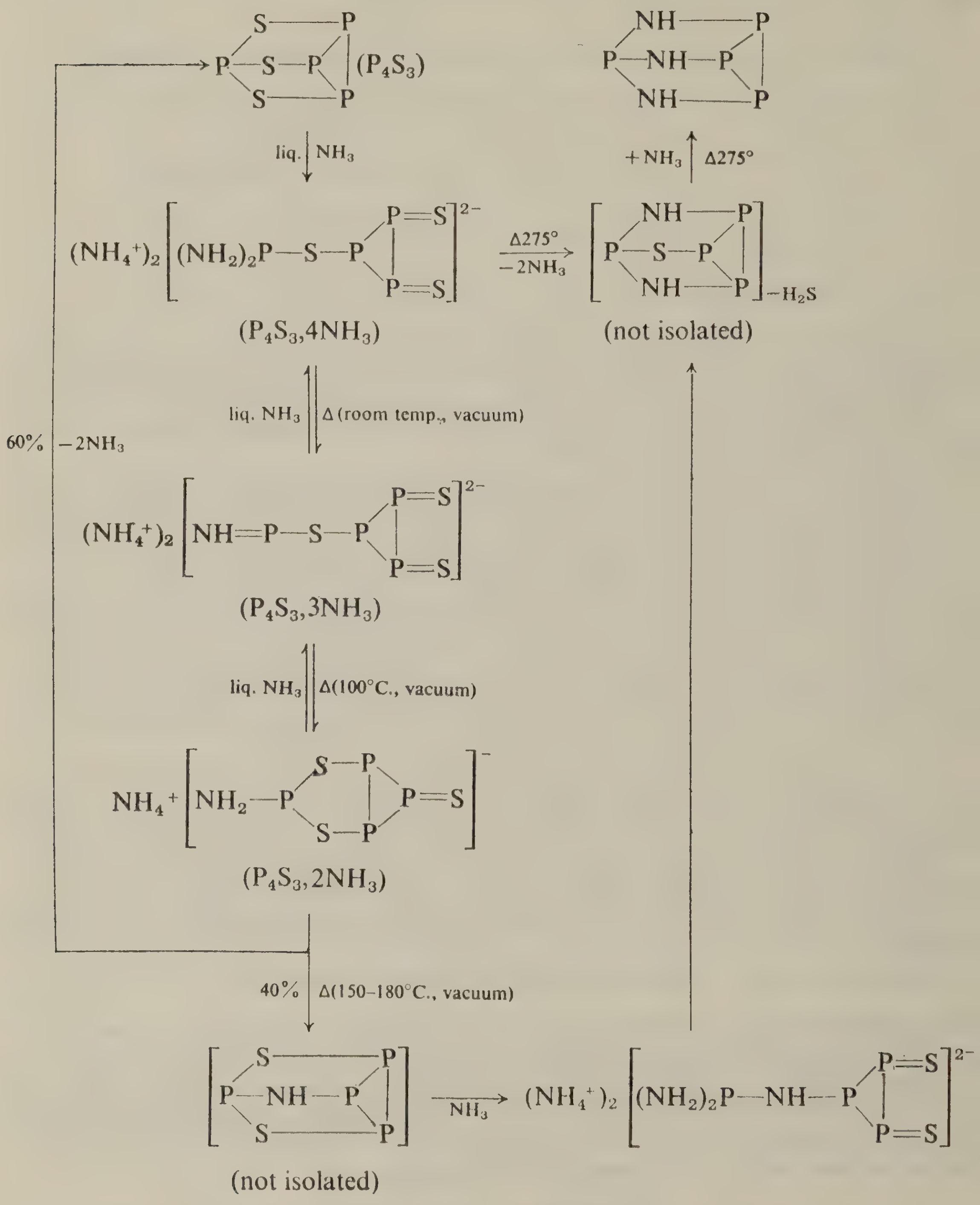


FIG. 4.—The ammonolysis of tetraphosphorus trisulphide

## PHOSPHORUS MONOSULPHIDE, PS

Two band systems can be detected in the ultraviolet emission spectrum of a helium discharge tube containing a small amount of tetraphosphorus trisulphide. One of these, which appears in the region 2700–3100 A. and shows a doublet splitting of 324 cm.$^{-1}$, is assigned to the species PS and the other, a singlet system in the region 2300–2750 A., to PS$^{+}$.[12–3] There is some evidence[14] that a compound of empirical formula PS is formed by the reaction of thiophosphoryl tribromide with magnesium in absolute ether:

$$2PSBr_3 + 3Mg \rightarrow (PS)_x + 3MgBr_2$$

It is described as a pale yellow powder, insoluble in the common organic solvents but containing small amounts of a crystalline material, $(PS)_n$, which forms lemon-yellow crystals from carbon disulphide. A gradual transformation from the amorphous to the crystalline form is claimed to occur on warming. The amorphous material decomposes at 135–140°C., the crystalline at 240°C. Both forms slowly hydrolyse in damp air, giving hydrogen sulphide and a mixture of hypophosphorous and phosphorous acids. Owing to its sparing solubility (80 mg./100 ml. at 23°C. in carbon disulphide) the mol. wt. of the crystalline form could not be determined, but in view of the ready interconversion of the phorphorus sulphides, even in solution, further confirmation of its structure and analysis is obviously desirable.

## TETRAPHOSPHORUS PENTASULPHIDE (PHOSPHORUS TETRITAPENTASULPHIDE), $P_4S_5$

### Preparation

Tetraphosphorus pentasulphide decomposes below its melting point[11]:

$$2P_4S_5 \rightleftharpoons P_4S_3 + P_4S_7$$

and hence cannot be obtained directly from a melt[1] although it results, together with the heptasulphide, from the extraction with carbon disulphide of a solidified melt of $P_4S_6$ composition.[33] It is best prepared following the method of Bouloch (Mellor, VIII, 1047), by irradiation of a solution of tetraphosphorus trisulphide and sulphur in carbon disulphide, using a trace of iodine as catalyst. The precipitated mass is washed with carbon disulphide, and recrystallized from the same solvent in a Soxhlet apparatus, all operations being conducted in an inert atmosphere.[8, 20]

### Physical Properties

Tetraphosphorus pentasulphide forms sulphur-yellow monoclinic crystals,[3] usually aggregated flat triangular plates, which are always twinned. The [*b*] axis is markedly uniterminal in appearance, showing that the crystals belong to the hemimorphic class of the monoclinic system.[6] A value of 10 g. per 100 g. $CS_2$ has been given for the solubility of the pentasulphide at 17°C.[39] This figure is possibly an estimate, since a solubility of 0·3–0·5 g. per 100 g. $CS_2$ has been independently determined by three other workers.[6, 11, 20] A solubility of 14·1 g. per 100 g. *o*-dichlorobenzene at 179°C. has also been recorded[8]; it was claimed that no decomposition was apparent from the infra-red spectrum of the recrystallized product.

The solid melts over the range 170–220°C.[1]: *X*-ray evidence shows that decomposition to $P_4S_3$ and $P_4S_7$ is already occurring in the solid at about 130°C.[11] Values of the density of the solid as determined directly[1] (2·17 g./c.c. at 25°C.) and from *X*-ray data[3] (2·15 g./c.c.) are in good agreement.

The unexpected and highly irregular structure of the tetraphosphorus pentasulphide molecule seems well established[3, 20] (see Fig. 1 and Tables I and II). Particularly interesting evidence is that given by the $^{31}P$ nuclear magnetic resonance spectrum of the solid, which shows three broad but well-spaced lines at $-200$, $-20$ and $+120$ p.p.m. relative to 85% orthophosphoric acid.[111] Optical activity, which would be expected in such a molecule, is not exhibited by solutions of the pentasulphide in carbon disulphide.[8] This could, however, be due to ready racemization or the existence of two racemic forms. The infra-red spectrum of the pentasulphide in carbon disulphide solution shows absorptions at 528 and 707 cm.$^{-1}$ [6] The '*d* values' of the three most intense lines in the *X*-ray diffraction pattern have been given as 4·76, 3·09, 1·78 A.[6] and 4·83, 3·09, 5·2 A.[8] An approximate value of $-50$ kcal./mole for the heat of formation has been estimated by differential thermal analysis[21] using the reaction:

$$P_4S_{5\text{cryst.}} + 2S_{\text{liq.}} \xrightarrow{155°\text{C.}} P_4S_{7\text{cryst.}}$$

### Chemical Properties

Although it is stable at room temperature, and can be recrystallised with suitable precautions, tetraphosphorus pentasulphide is the most reactive and unstable of the four authenticated phosphorus sulphides. In carbon disulphide solution at 170°C. it appears to exist in a mobile equilibrium with the tri- and hepta-sulphides.[11] The pentasulphide is also very readily hydrolysed and crystals of the compound decompose fairly quickly unless protected from moisture. As in the case of the tri- and hepta-sulphides, the products of hydrolysis include thio-phosphates, -phosphites and -hypophosphites.[34, 97, 109] The reaction with ammonia has been closely studied.[23] The sulphide dissolves readily in liquid ammonia and on evaporation of the solution at $-33$°C. a canary yellow hygroscopic solid of empirical formula $P_4S_5,6NH_3$ can be recovered. This product, which forms ammonia-insoluble salts with complex ammono-cations such as $[Cr(NH_3)_6]^{3+}$ or $[Ni(NH_3)_4]^{2+}$, contains the tribasic anion $[P_4S_5(NH_2)_3]^{3-}$, and probably has some such structure as

$$(NH_4)_3{}^+[(NH_2)_2P\text{–}S\text{–}P(S)\text{–}P(S)\text{–}P(S)NH_2]^{3-}$$

When heated *in vacuo* to +70°C., this compound decomposes with loss of ammonia giving a golden yellow solid of formula $P_4S_5,4NH_3$. At higher temperatures (140°C.) this loses hydrogen sulphide and more ammonia to give $P_4S_3(NH)_2$, presumably analogous to $P_4S_5$, which in its turn decomposes at 180°C. into tetraphosphorus trisulphide and a colourless involatile solid of empirical formula $P_4S_3(NH)_7$. The last compound, formally analogous to $P_4S_{10}$, is insoluble in carbon disulphide or liquid ammonia and is hydrolysed by water or dilute acids to phosphoric acid, hydrogen sulphide and ammonia. It is stable to alkalis even on boiling. Further treatment with ammonia gas at 750°C. converts it into triphosphorus pentanitride, $P_3N_5$. The decomposition of $P_4S_5,4NH_3$ gives rise also to minor quantities of tetraphosphorus decasulphide, heptasulphide and heptasulphide tri-imide (colourless and insoluble in carbon disulphide) which may be separated by taking advantage of their differing volatilities and solubilities. Little else is known of the reactions of tetraphosphorus pentasulphide. A study of its reaction with ethanol[36] gave no identifiable products, and was in any case probably carried out with a fusion product of phosphorus and sulphur analysing as $P_4S_5$. Such a product would be a mixture of tetraphosphorus tri- and heptasulphides with varying amounts of the metastable '$\beta$-heptasulphide' phase.

## TETRAPHOSPHORUS HEXASULPHIDE ($P_4S_6$)

### Preparation

Several early claims for the existence of a compound with an empirical formula $P_4S_6$ (or $P_2S_3$) were discounted by other authors (Mellor, VIII, 1052), since melts of this composition could readily be separated into tetraphosphorus trisulphide and heptasulphide by sublimation or crystallization. Beeli[33] showed that the products of solvent extraction of a sulphide sample of composition $P_4S_6$ were in fact tetraphosphorus pentasulphide and heptasulphide. This was later confirmed[8–9] and the same workers also showed that a sulphide of identical composition formed from phosphorus trichloride and liquid hydrogen sulphide at room temperature[7] could be resolved in the same way.

Fresh evidence is, however, provided by an *X*-ray study[11] of melts with compositions in the range $P_4S_5$ to $P_4S_{6\cdot9}$. If these are made up from tetraphosphorus trisulphide and sulphur or the heptasulphide, the product on cooling has a unique *X*-ray powder diagram, unlike that of any known sulphide. Melts made from red phosphorus and sulphur also contain this new phase, but are mixed with other sulphides unless catalytic amounts of iodine are added, when the new phase alone is formed. The reaction product of phosphorus trichloride and hydrogen sulphide also shows the same diffraction pattern, though there is some evidence of other material being present.

### Physical Properties

Tabular lemon-yellow crystals of the new phase can be obtained by slow cooling of melts with compositions near to $P_4S_6$. Such crystals sinter at 235°C. and melt with decomposition between 250° and 290°C. The strongest powder lines have *d* values 5·72(s), 3·62(ms), 2·95(ms) and 2·86(s) A. The mother liquor on solidification shows the same diffraction pattern, although its melting point is lower, and this evidence of segregation, together with the wide composition range over which the phase is formed, suggests that it may be of variable composition. This is supported by the observation that there is a regular increase in the *X*-ray powder line spacings, corresponding to a decrease in lattice dimensions, with decreasing sulphur content.

The crystals have an orthorhombic unit cell, of space group *Pbcn* with cell lengths $a = 8{\cdot}14 \pm 0{\cdot}04$, $b = 11{\cdot}43 \pm 0{\cdot}03$, $c = 11{\cdot}39 \pm 0{\cdot}03$ A. and density 2·09 g./c.c.[108] With 4 molecules per unit cell, the statistical composition would be $P_4S_{6\cdot6}$, and the *X*-ray data cannot be reconciled with any simple stoicheiometry. Analysis of specimen crystals is difficult because of their instability, but again suggests that they contain more sulphur than the $P_4S_6$ melt from which they are formed. The problem has been resolved by an *X*-ray investigation which shows that the new phase comprises molecules of $P_4S_7$ of the same type as those found in the stable ($\alpha$) phase of this composition. However, molecules of the new ($\beta$) phase, unlike $\alpha$-$P_4S_7$, have an exact crystallographic 2-fold symmetry axis, and there is crystallographic evidence for a deficiency of sulphur in the apical positions, which accounts for the peculiar composition. The molecular dimensions are those of $\alpha$-$P_4S_7$, except that the P–P bond has a more normal length of 2·26 A.[108]

### Chemical Properties

'$\beta$-Tetraphosphorus heptasulphide' is stable only over the narrow temperature range 200–250°C. Rapid chilling from 270°C. of a partly melted specimen shows $\alpha$-tetraphosphorus heptasulphide to be present, though normally such melts supercool sufficiently for the $\beta$-heptasulphide to separate. Below 200°C. the $\beta$-heptasulphide also decomposes to the trisulphide and $\alpha$-heptasulphide, but the process is sufficiently slow (about 1 day at 195°C.) for the $\beta$-heptasulphide to be cooled with little decomposition to room temperature, where it may be preserved for several months. Sublimation decomposes the sulphide into $\alpha$-tetraphosphorus heptasulphide and trisulphide, whilst treatment with carbon disulphide gives these two sulphides and, in addition, tetraphosphorus pentasulphide.[11] It is claimed that a melt of $P_4S_6$ composition is more effective in reducing phenols to hydrocarbons than trisulphide or $\alpha$-heptasulphide, either alone or in admixture.[102]

## TETRAPHOSPHORUS HEPTASULPHIDE (PHOSPHORUS TETRITAHEPTASULPHIDE), $P_4S_7$

### Preparation

Tetraphosphorus heptasulphide can be obtained from solidified melts of composition between $P_4S_6$ and $P_4S_8$ by extraction with carbon disulphide in a Soxhlet apparatus, when the sparingly soluble heptasulphide crystallizes in the flask.[33] The preparative procedure of Mai (Mellor, VIII, 1053) has been confirmed by later workers.[8–9] It involves heating appropriate mixtures of sulphur and phosphorus or phosphorus sesquisulphide in boiling xylene, in the presence of a trace of iodine, followed by recrystallization of the product from carbon disulphide. Tetraphosphorus heptasulphide is also formed by the action of sulphur on diphosphorus tetraiodide, or phosphorus with a trace of iodine, in cold carbon disulphide solution.[100] Several procedures have been described for the commercial production of this sulphide, both from the elements[17–8] and by reaction of mixtures of sulphur and ferrophosphorus.[40] However, it is not widely used commercially, probably because of its ready hydrolysis and the poorly defined character of its organic reaction products.[10, 41]

## Physical Properties

Crystals of tetraphosphorus heptasulphide are usually very small and often fragmentary. They are squat and columnar along the [*c*] axis, with poorly developed end faces. The refractive indices are $\alpha = 1{\cdot}465$ (along the crystal [*b*] axis), $\beta = 1{\cdot}48$, $\gamma = 1{\cdot}49$, with $\gamma \wedge [c] = 10°$.[6] They are almost white with a faint yellowish tinge.[8] The sulphide melts at 310°C. and boils at 523°C.[23] (cf. m.p. 308 ± 1°C., b.p. 529 ± 2°C.[106]). Values of +17·5 kcal./mole for the heat of fusion, and +20·0 kcal./mole for the heat of vaporisation, have been estimated by differential thermal analysis.[21] Later values of 22·4 ± 0·6 kg.-cal./mole and 27·9 ± 1·0 e.u./mole have been recorded for the heat and entropy of vaporization respectively.[106] The density, 2·19 g./c.c., calculated from *X*-ray diffraction data[4] agrees exactly with an earlier experimental value.[42]

The structure of the tetraphosphorus heptasulphide molecule has been established by *X*-ray diffraction[4] (see Fig. 1 and Tables I and II). The lengths of the P–S and P═S bonds agree well with the corresponding bonds in the $P_4S_{10}$ molecule but, as previously pointed out, there is no analogy for the unusually long P–P bond.

The infra-red spectrum of the heptasulphide in carbon disulphide solution shows absorptions at 452, 480, 509, 538, 698 and 708 cm.$^{-1}$ [6]

The '*d* values' of the strongest lines in the *X*-ray powder photograph are given as 2·92, 3·10, 6·21[8]; 2·90, 6·30, 6·40[6]; 2·92, 3·09, 6·19 A.[11] Tetraphosphorus heptasulphide is very sparingly soluble in carbon disulphide (Mellor, VIII, 1054) and even in *o*-dichlorobenzene at 179°C. only 1·32 g. of sulphide dissolves in 100 g. of solvent.[8]

By the differential thermal analysis of heated mixtures of $P_4S_{3\text{cryst.}} + 4S_{\text{liq.}}$ and $4P_{\text{red}} + 7S_{\text{liq.}}$ it was established that between 160° and 275°C. formation of heptasulphide is almost complete. Values of the enthalpy of formation derived from the observed heats of reaction are in good agreement, the mean value being 71 ± 10 kcal./mole.[21]

## Chemical Properties

Cold water attacks tetraphosphorus heptasulphide slowly, with evolution of hydrogen sulphide. In hot water the reaction is rapid, and phosphine and hydrogen occur among the products.[41] The electrical conductivity of a slurry of tetraphosphorus heptasulphide in water increases very rapidly with time, eventually reaching a constant value which is nearly twice as great as that given by the same amount of the decasulphide.[33] The sulphide also hydrolyses rapidly in dilute acids or alkalis, the final products being hydrogen sulphide, phosphine and phosphorus oxyacids (see Table IV).

*Table IV.—Alkaline Hydrolysis Products of Tetraphosphorus Heptasulphide*

| Reference | Atoms of P per mole $P_4S_7$ determined as: | | | | |
|---|---|---|---|---|---|
| | $PH_3$ | $H_3PO_2$ | $H_3PO_3$ | $H_3PO_4$ | Unaccounted for |
| 1 | 0·1 | 0·1 | 1·5 | 2·3 | — |
| 10 | — | 0·95 | 0·87 | 2·03 | 0·15 |

Under milder conditions intermediate hydrolysis products can be isolated. Thus on a paper chromatogram, using the alcoholic trichloroacetic acid solvent of Ebel, tetraphosphorus heptasulphide gave a number of spots, which by their chemical behaviour and by comparison with standards, were identified with fair certainty as mono- and di-thiohypophosphite, monothiophosphite and monothiophosphate.[34] The mechanism proposed for their formation is shown in Fig. 5.

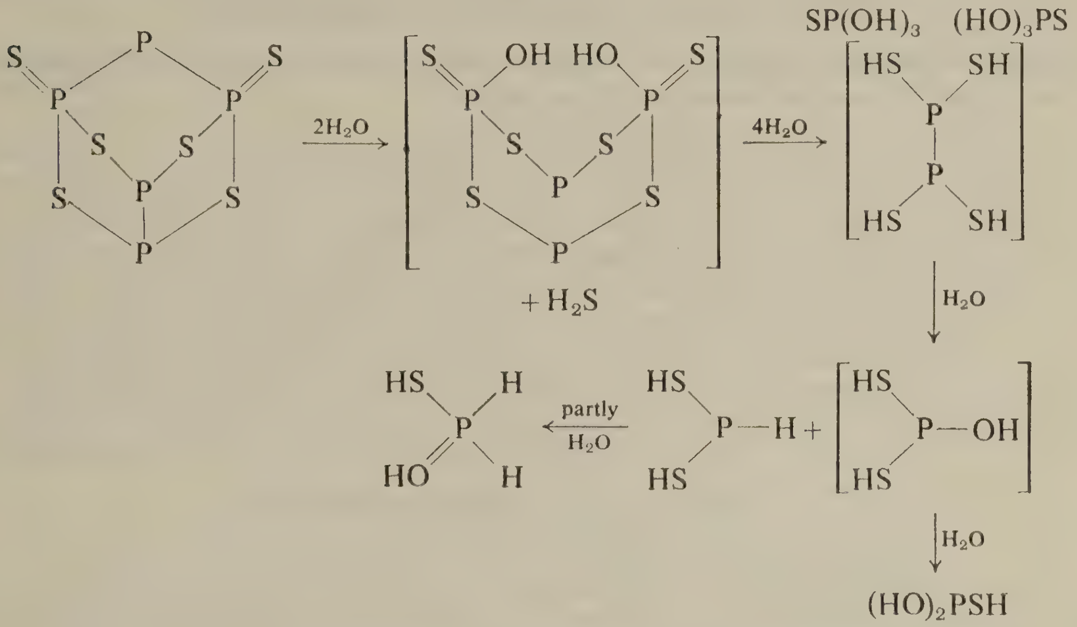


FIG. 5.—The hydrolysis of tetraphosphorus heptasulphide

Alkaline hydrolysis of the lower phosphorus sulphides in the presence of hydrogen peroxide, on the other hand, gives a number of oxyacids.[97, 109] Some of these retain P–P bonds present in the parent sulphides. The anions may be detected and determined by paper chromatography, and are present in the proportions shown in Table V.

*Table V.—Oxidative Hydrolysis Products of Lower Phosphorus Sulphides*

| Sulphide | Anion (Percentage based on initial P added) | | | | | |
|---|---|---|---|---|---|---|
| | $(HPO_3)^2$ | $(PO_4)^{3-}$ | $(P_2O_7)^{4-}$ | $(P_2O_6)^{4-}$ | $(PO_3.PO_2.PO_3)^{5-}$ | $(PO_3.O.PO_2.PO_3)^5$ |
| $P_4S_3$ | 10 | 35 | 5 | 20 | 15 | 15 |
| $P_4S_5$ | 10 | 40 | 10 | 25 | 5 | 10 |
| $P_4S_7$ | 10 | 55 | 5 | 25 | — | 5 |

The products of ammonolysis can also be explained by reference to the structure of the sulphide.[43] One mole of the sulphide reacts with 8·5 moles of liquid ammonia at −33°C. according to the equation:

$$2P_4S_7 + 17NH_3 \rightarrow (NH_4)_3PS_4 + 2(NH_4)_2PS_3NH_2 + (NH_4)_3(P_3S_3(NH)_3) + NH_4P_2SN$$

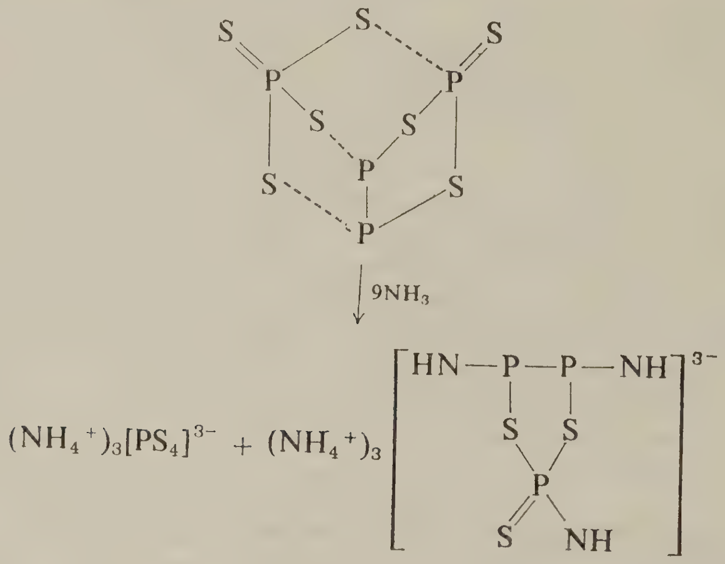
The mechanism was established by quantitative isolation of $(NH_4)_3PS_4$ and $(NH_4)_2PS_3NH_2$, which differ in their solubility in liquid ammonia. The highly soluble $(NH_4)_3(P_3S_3(NH)_3)$ was isolated as the double salt $Ni(NH_3)_4NH_4(P_3S_3(NH)_3)$, in almost theoretical yield. The results accord with the roughly equal participation of the two routes of ammonolysis shown in Fig. 6.

Tetraphosphorus heptasulphide does not react with bromine or iodine in carbon disulphide solution. In an aqueous medium reaction is rapid, roughly 30 atoms of bromine being taken up per mole of sulphide. Sulphur was the only product identified.[1]

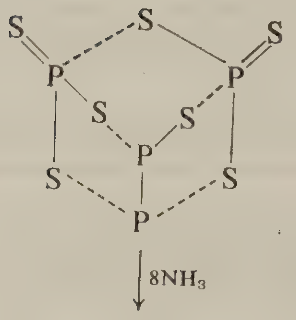
As with the other lower sulphides, the organic reactions of the heptasulphide have been little studied. The lower alcohols yield a variety of products, including di- and trialkyl phosphorodithioates, $(RO)_2PSSH$ and $(RO)_2PS(SR)$, and dialkyl phosphorothioites, $(RO)_2PSH$.[36, 83] Grignard reagents alkylate the phosphorus, largely according to the equation:

$$P_4S_7 + 12RMgX \rightarrow 3R_3P + R_3PS + 6MgS + 6MgX_2$$

although dialkylphosphinodithioic acids, $R_2PS_2H$, and alkylphosphonotrithioic acids, $RPS_2SH$, may be formed as by-products.[37]



Route 1



$$2(NH_4{}^+)_2[PS_3NH]^{2+} + (NH_4{}^+[P_2SN]^-)$$

not isolated
probably polymeric

Route 2

FIG. 6.—The ammonolysis of tetraphosphorus heptasulphide

## TETRAPHOSPHORUS DECASULPHIDE (PHOSPHORUS TETRITADECASULPHIDE, PHOSPHORUS PENTASULPHIDE), $P_4S_{10}$

### Preparation

Tetraphosphorus decasulphide is commercially the most important of all the phosphorus sulphides, and for this reason it has been extensively studied, but certain aspects of its chemistry remain to be explained. Of the two forms reported by Stock to occur in the commercial sulphide (Mellor, VIII, 1055) only that with the lower solubility in carbon disulphide has been characterized.

A laboratory preparation of the sulphide by reaction between white phosphorus and sulphur in an organic solvent has been described[44] but the preferred method is still that of Stock,[45] involving the recrystallization of a solidified melt. Purification is assisted if the crude sulphide is caused to react with ethanol until half is dissolved. The residue requires little recrystallization to give pure tetraphosphorus decasulphide.[46] Isotopically labelled tetraphosphorus decasulphide has been obtained by exchange reaction of the inactive sulphide with carrier free $H_3{}^{32}PO_4$. The product retained its specific activity through repeated recrystallizations from carbon disulphide.[47]

A continuous process for the manufacture of the decasulphide has been described.[17, 41, 112] Liquid white phosphorus and sulphur in the correct proportions are fed continuously to a stirred heel of molten sulphide. The product overflows to a mixer-finisher for final adjustment of composition, and thence to a water-cooled drum flaker. In another process the heat of reaction is used to assist the distillation of the sulphide.[18] A product of improved colour obtained by introduction of oxidizing agents during this distillation[19] probably contains oxysulphides. The use of purified phosphorus is also claimed to give a product of good colour.[113]

Processes have been described for the manufacture of tetraphosphorus decasulphide from ferrophosphorus, a by-product of the electric furnace manufacture of phosphorus.[40, 48] The reactions concerned are:

$$4Fe_2P + 18FeS_2 \rightarrow P_4S_{10} + 26FeS$$
$$4Fe_2P + 18S \rightarrow P_4S_{10} + 8FeS$$

The manufacture of phosphorus sulphides, including the pentasulphide, by carbon reduction of phosphates in the presence of sulphur has also been claimed.[49] Finally it has been reported that tetraphosphorus decasulphide is formed by reaction of thiophosphoryl chloride with hydrogen sulphide in the presence of a tertiary base at 120–130°.[114]

### Physical Properties

Pure tetraphosphorus decasulphide forms well developed triclinic crystals. The most common habit is a combination of prismatic and pyramidal forms. Some crystals are lath- or needle-shaped and a very few rhomboidal, but all give the same *X*-ray unit cell measurements, showing that only one crystalline form is present. All the principal refractive indices seem to be less than 1·50, and the optical sign is positive. The crystals are weakly birefringent, as would be expected from the crystal structure, in which highly symmetrical molecules are arranged in a near-cubic lattice.[4, 6] A density of 2·11 g./c.c. deduced from *X*-ray diffraction data[4] is in good agreement with the experimental value of 2·09 g./c.c.[45] Tetraphosphorus decasulphide melts at 288 ± 1°C. and boils at 514 ± 2°C. Its enthalpy and entropy of vaporization are 21·3 ± 0·6 kcal./mole and 27·2 ± 1·2 e.u./mole, respectively.[106]

The structure of the tetraphosphorus decasulphide molecule[6] is entirely analogous to that of the H form of phosphoric oxide, $P_4O_{10}$[50] (see Fig. 1 and Tables I and II). The molecule is symmetrical, within the limits of experimental error. The infra-red spectrum[6] shows absorptions at 535 and 695 cm.$^{-1}$ The $^{31}P$ nuclear magnetic resonance spectrum of the solid sulphide, measured by a rapidly rotating specimen technique, shows a single line at −45 p.p.m. relative to 85% orthophosphoric acid (cf. −16 p.p.m. for $P_4O_6S_4$ and +48 p.p.m. for $P_4O_{10}$).[111] The '*d* values' of the strongest lines in the *X*-ray powder diagram are given as 2·86, 2·92, 4·04 A.[8]; 2·86, 2·88, 2·95 A.[6]

The variation of heat capacity with temperature between 30 and 350°K. is smooth, and shows no anomalies characteristic of a transition to a plastically crystalline phase, such as are observed with tetraphosphorus trisulphide. The entropy of $P_4S_{10}$ at 298·15°K. is 91·24 g.-cal./(mole °K.) and the molal heat capacity 70·74 g.-cal./°K.[107]

The solubility of tetraphosphorus decasulphide in both carbon disulphide and *o*-dichlorobenzene, is intermediate between that of the heptasulphide and of the trisulphide. The latter solvent dissolves 6·03 g. of decasulphide/100 g. of solvent at

179°C.[8] The decasulphide is also slightly soluble in chloronaphthalene and trichlorobenzene.[41]

### Other Forms of 'Phosphorus Pentasulphide'

The form of phosphorus decasulphide of which the properties have been described above is obtained in greatest yield by slow cooling of melts having a composition in the $P_4S_{10}$ region. It is highly crystalline, with a characteristic infra-red spectrum, and low solubility in carbon disulphide (0·22% at 17°C.). Its mol. wt. as determined by cryoscopy is in good agreement with the formula $P_4S_{10}$ (=444). Quick cooling of $P_4S_{10}$, from either melts or the vapour, gives a product which appears to be a mixture of this normal $\alpha$ form with other crystalline and amorphous forms. These have a much higher solubility in carbon disulphide (up to 4%), their infra-red spectra exhibit satellite absorptions around the main maxima at 535 and 695 cm.$^{-1}$ and mol. wt. determinations give values below 400. An *X*-ray study also reveals differences. Thus the *X*-ray powder diagram of pure $\alpha$-decasulphide exhibits a doublet (6·04 and 5·87 A.) and a singlet (3·67 A.), which in very quickly cooled 'pentasulphide' are replaced by a singlet (5·91 A.) and a doublet (3·81 and 3·76 A.), respectively. Intermediate cooling rates give intermediate values for the splitting.[6, 41, 51]

The pure $\alpha$-decasulphide gives a pale yellow solution in carbon disulphide, but that of the 'quickly-cooled' material is intensely yellow. The solid recovered from the latter solution is yellowish white and melts at about 250°C.[6] It reacts more rapidly and exothermically with aliphatic alcohols than does the $\alpha$ form and, remarkably, the products appear to be fewer in number.[83] The proportion of the reactive form can be raised by increasing the rate of cooling of the melt through the temperature range around the melting point, i.e. 280–260°C.[51–2] The reactivity of a quickly-cooled melt can also be reduced, and the proportion of $\alpha$-decasulphide correspondingly increased by reheating the solid for various times at temperatures between 150° and 270°C.[53, 105] In view of their high solubility and reactivity, these reactive forms of the decasulphide are not likely to be highly polymeric in character, though there is no evidence for the suggestion[41] that they contain diphosphorus pentasulphide, $P_2S_5$.

### Chemical Properties

The hydrolysis of tetraphosphorus decasulphide, if allowed to go to completion, results in the formation of phosphoric acid and hydrogen sulphide with only traces of other phosphorus compounds (see Table VI and more recent results[81] in Fig. 7).

*Table VI.—Alkaline Hydrolysis Products of Tetraphosphorus Decasulphide*

| Reference | Atoms of P per mole $P_4S_{10}$ expressed as: | | | | |
|---|---|---|---|---|---|
| | $PH_3$ | $H_3PO_2$ | $H_3PO_3$ | $H_3PO_4$ | Unaccounted for |
| 1 | — | 0·4 | — | 3·2 | 0·4 |
| 10 | — | — | — | 4 | — |

The polythiophosphoric acids, $H_3PS_4$, $H_3PS_3O$, $H_3PS_2O_2$ and $H_3PSO_3$, are probably involved as intermediates. These acids are all unstable, and can exist only in dilute solution, but their alkali metal salts are more stable, the stability decreasing with increasing sulphur content.[54] Only phosphorothioate could be identified in the hydrolysis products of the sulphide on a paper chromatogram under acid conditions.[34]

The decasulphide reacts with liquid ammonia at −33°C. to give a mixture of diammonium phosphoramidotrithioate, $(NH_4)_2PS_3NH_2$, and diammonium phosphoronitridodithioate, $(NH_4)_2PS_2N$, which can be separated using their differing solubilities

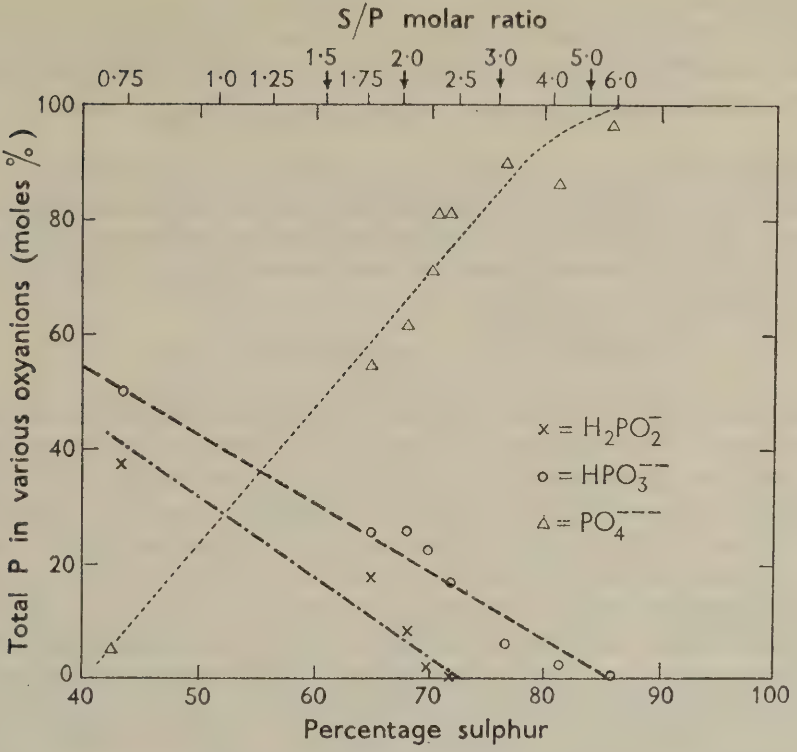
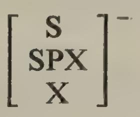


FIG. 7.—Hydrolysis products of phosphorus–sulphur compositions

in liquid ammonia, the former being sparingly, and the latter readily, soluble at −78°C.[43] This contrasts with the findings of Stock[55] who, working at room temperature, obtained in addition to $(NH_4)_2PS_2N$, triammonium phosphorimidotrithioate, $(NH_4)_3PS_3NH$, and tetra-ammonium diimidopentathiopyrophosphate,

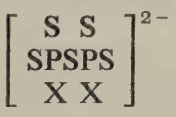
$$((NH_4S)_2P(NH))_2S$$

Tetraphosphorus decasulphide does not react with iodine in carbon disulphide, and gives only a slight reaction with bromine under similar conditions.[1] Phosphoric oxide reacts with the decasulphide giving oxysulphides (see page 406). The interaction of certain metal salts with tetraphosphorus decasulphide in polar media yields anionic substituted thiophosphates of types 1–3



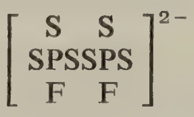
$$\left[\begin{matrix} \mathrm{S} \\ \mathrm{SPX} \\ \mathrm{X} \end{matrix}\right]^-$$

1



$$\left[\begin{matrix} \mathrm{S\ S} \\ \mathrm{SPSPS} \\ \mathrm{X\ X} \end{matrix}\right]^{2-}$$

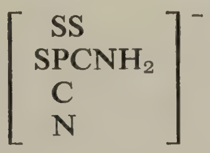
2



$$\left[\begin{matrix} \mathrm{S\ \ \ S} \\ \mathrm{SPSSPS} \\ \mathrm{F\ \ \ F} \end{matrix}\right]^{2-}$$

3

The type of anion formed depends on the solvent employed and the isolation procedure. Thus sodium fluoride or azide in water yield divalent anions of type 2, while in acetonitrile the products are predominantly of type 1. Sodium cyanide under these conditions appears to yield the species



$$\left[\begin{matrix} \mathrm{SS} \\ \mathrm{SPCNH_2} \\ \mathrm{C} \\ \mathrm{N} \end{matrix}\right]^-$$

These anions, the structures of which are not yet rigorously established, show fairly good stability towards acids and bases. Hydronium salts have been prepared in several cases, and those of the $S_2P(N_3)_2$ and $S_2PF_2$ anions can be distilled *in vacuo* with little decomposition.[116]

ORGANIC REACTIONS

The organic reactions of tetraphosphorus decasulphide have been extensively studied. With alcohols[56] the corresponding dialkyl phosphorodithioates are formed:

$$P_4S_{10} + 8ROH \rightarrow 4(RO)_2PSSH + 2H_2S$$

Dialkyl sulphides, mercaptans, sulphur, 'phosphorus polysulphides',[57] tetra-alkyl trithiopyrophosphates[46] and other organic compounds containing phosphorus and sulphur[83] occur as by-products either from the reaction or from the decomposition of the primary products. Phenols also give phosphorodithioates[58] while tetrathioates result from thiophenols or mercaptans[59]:

$$8RSH + P_4S_{10} \rightarrow 4(RS)_2PSSH + 2H_2S$$

Orthoformates and trithio-orthoformates give phosphorodithioates and phosphorotetrathioates respectively.[60] Primary and secondary amines yield a variety of phosphorothioic amides, dealkylation occurring in some instances.[61–2] Carboxylic amides, on the other hand, form complexes of unknown structure, which decompose on heating to give the corresponding thioamides. Tetraphosphorus decasulphide reacts with aromatic hydrocarbons to give a variety of products in which both phosphorus and sulphur may be attached to the aromatic nucleus. Under controlled temperature conditions, unstable derivatives of the empirical formula $ArPS_2$ can be isolated. These normally exist in the dimeric form, and polymerize further on heating, while on hydrolysis they yield the corresponding phosphonic acids, $ArPO(OH)_2$.[38, 63] In the presence of aluminium chloride the reaction takes a different course, and diarylphosphinodithioic acids are formed in good yield[64]:

$$8ArH + P_4S_{10} \rightarrow 4Ar_2PSSH + 2H_2S$$

Less well-defined products, which result from the action of the decasulphide on a variety of aliphatic and alicyclic hydrocarbons, find application as lubricant additives.[65]

Tetraphosphorus decasulphide has been widely used for the replacement of oxygen by sulphur in organic oxygen-containing compounds. Examples of such reactions include the preparation of thioamides from amides,[66] thioketones from aliphatic ketones,[67] and thioaldehydes from aldehydes.[68] Thiocholesterol,[69] thiopyran,[70] thiouracils,[71] mercaptopurines[103] and thiopyridones[72] have been made in a similar way. One, two or three of the oxygen atoms in barbituric acids can be replaced by sulphur using tetraphosphorus decasulphide under varying conditions.[73] Some alcohols or ketones, such as $C_6H_5CH_2NHCH_2CH_2OH$,[74] $RCOCHR'COOR''$[75] and $C_6H_5COCH_3$[68] undergo somewhat more complex thiation reactions leading to cyclic derivatives.

Tetraphosphorus decasulphide reacts with Grignard reagents in anhydrous ether. Hydrolysis of the product yields a mixture of compounds in which alkylphosphonodithioic acids, $RPS(OH)(SH)$, dialkylphosphinodithioic acids, $R_2PSSH$, and trialkylphosphine sulphides, $R_3PS$, predominate successively as the proportion of Grignard reagent to sulphide is increased in the original reaction.[76–7]

## HIGHER SULPHIDES OF PHOSPHORUS

Tetraphosphorus decasulphide is the highest authenticated sulphide of phosphorus. However, the physical properties of melts having an S/P molar ratio higher than 2·5 do not alter monotonically with the proportions of the elements present,[78–9, 104] and this suggests that some type of combination is occurring between the decasulphide and sulphur when these are heated together. Several pieces of evidence support this hypothesis. A clearly defined maximum in the melting point–composition diagram for the phosphorus sulphides (Fig. 3) occurs at a sulphur content of 84–86% (see above, page 414). The solubility of phosphorus sulphide melts in carbon disulphide goes through a minimum at a similar sulphur content. A series of mixtures of tetraphosphorus decasulphide and sulphur was heated to 400°C. in an inert atmosphere, cooled, kept for one week and ground. A 25 g. sample of each was agitated twice at room temperature for 30 min. with two separate 200 ml. portions of carbon disulphide; the weights of sulphide extracted are shown in Table VII.[80]

*Table VII.—Solubility of Phosphorus Sulphide Melts in Carbon Disulphide*

| Sulphur content of melt (%) | Solubility in 400 ml. $CS_2$ (g.) |
|---|---|
| 72·18 | 4·3 |
| 75·0 | 3·3 |
| 79·13 | 2·0 |
| 86·10 | 0·7 |
| 93·04 | 10·6 |

Experiments at higher sulphur contents are in general agreement, showing a decreasing solubility from 100 to 93% S.[79]

A study of the hydrolysis of a similar series of phosphorus sulphide melts has given supporting evidence. Melts of S/P ratio around 0·75 give hypophosphite, phosphite and phosphate on hydrolysis. As the S/P ratio increases, the proportion of hypophosphite and phosphite decreases, until at $S/P \simeq 2{\cdot}5$ hypophosphite is no longer observed. Phosphite is still formed, however, and can be detected in the hydrolysates of melts up to $S/P = 5$–$6$ (see Fig. 7).[81]

Unlike mechanical mixtures of sulphur and decasulphide, melts with S/P ratios higher than 2·5 (72·7% S) cannot be completely separated by extraction with benzene or carbon disulphide. Melts containing from 72 to 84% sulphur give a solution containing phosphorus decasulphide; between 85 and 89% the solution contains almost pure sulphur. In both cases the residue from repeated extraction[6] has a composition nearer to $PS_6$; similar shifts in composition have been observed by later workers.[79]

Material having a composition in the range 85·5–87·5% S is non-crystalline (by *X*-ray examination) and is almost insoluble in benzene or carbon disulphide. Unsuccessful attempts have been made to anneal it into a crystalline form by cooling it slowly from various temperatures below its melting point. It melts to a viscous liquid, from which threads can be drawn by touching it with a glass rod and pulling away. The *X*-ray diffraction diagrams of these threads are typical of glasses or unoriented polymers. The diffraction rings which they exhibit show no orientation effects from which a repeat distance along the axis of the thread might be inferred. Spacings of 3·03, 5·45 and possibly 11·47 A. can be calculated from the diffraction rings,[6] but these do not correspond to spacings observed in the known phosphorus sulphides, nor to those in plastic sulphur.[82] There is no evidence of crystallization in threads which have been aged for periods of up to 35 days.[6]

It may be assumed that the polymeric sulphides $(PS_{5\cdot5})_x$ and $(PS_7)_x$, obtained by the reaction of tetrathiophosphoric acid with sulphur dichloride and disulphur dichloride, respectively, are of similar nature. These are described as plastic yellow products, stable at room temperature but decomposing above 200°C. They are insoluble in water or organic solvents, and are decomposed by alkalis.[98, 110]

This evidence, though circumstantial, suggests the existence of a phase of variable composition with an empirical formula approximating to $PS_6$. There is, however, no reason to suppose that such a phase, even if it exists, would have a simple molecular structure. Indeed its properties are just those which would be expected if it were a random network polymer of the type discussed by Van Wazer.[78, 83] The clearest evidence for such polymer formation is afforded by the viscosity–temperature curves of phosphorus sulphide melts[83] as shown in Fig. 8. Pure liquid white phosphorus has a low viscosity which increases only slightly with decreasing temperature. Similar behaviour is shown by sulphide melts of S/P ratio 1·00 and 1·25, though their viscosity reaches very much higher values, suggesting a degree of cross-linking. However, melts with an S/P ratio above about 2 show a maximum in their viscosity–temperature curves similar to that observed in the case of liquid sulphur, where such behaviour has been ascribed to the presence of polymeric molecules of high mol. wt. It is found that minor variations in composition exert a marked effect on the viscosity of phosphorus sulphide melts. The maximum value of the viscosity increases with increasing sulphur content over the S/P range 2–3, while the temperature of the viscosity maximum falls. The viscosity of such melts is little affected by additives which reduce the viscosity of pure sulphur, and their flow behaviour is Newtonian at temperatures between 300 and 500°C., suggesting that the rate of molecular reorganization under these conditions is rapid compared with the mean relaxation time. Nuclear magnetic resonance spectroscopy shows that even in melts of S/P ratio as low as 1·00 or 1·25, only 59 and 33%, respectively, of the total phosphorus is present in the form of discrete $P_4S_3$ molecules. Several other resonance peaks seen in the spectra evince the presence of phosphorus atoms in a number of unidentified environments. It is evident from consideration of this evidence that amorphous phosphorus sulphides, particularly those of S/P ratio ⩽ 1·8, contain not only small 'cage molecules' of the type already described, but also chains both straight and branched, and rings of sulphur atoms all cross-linked through phosphorus. A complementary study of the kinetics of alcoholysis of phosphorus sulphide melts of varying composition, and the varying nature of the products obtained therein, was in broad general agreement with this picture.[83]

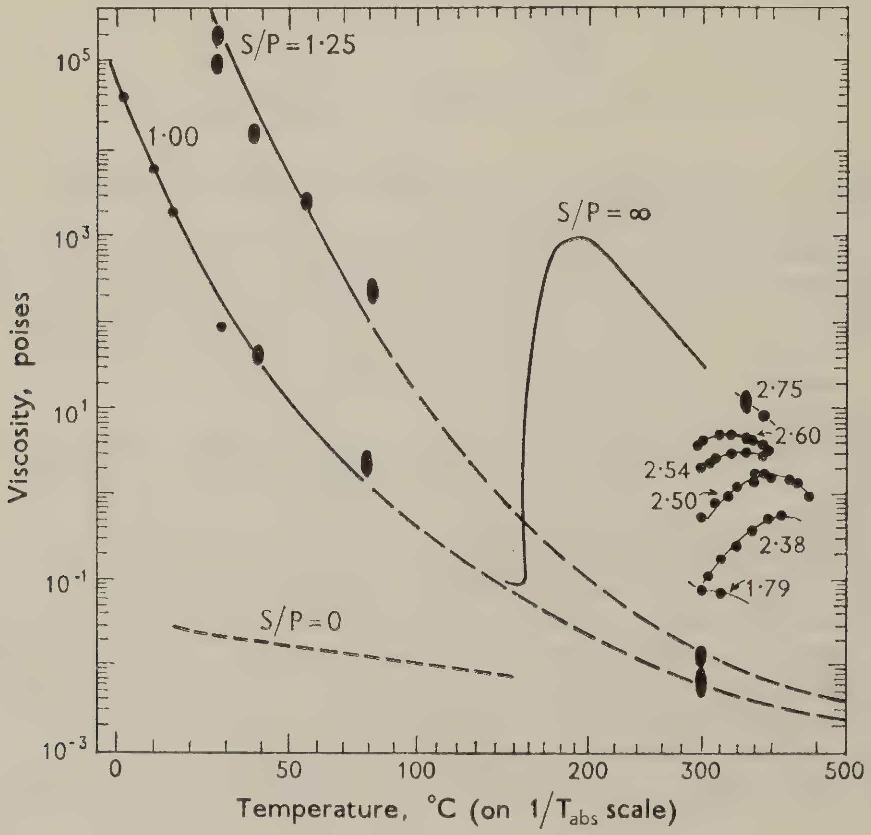


FIG. 8.—Viscosity of various phosphorus sulphides

Further evidence of the polymeric nature of phosphorus sulphide melts has been obtained from a study of their elasticity. Pure plastic sulphur (S$\mu$) yields relatively weak fibres, but the addition of a few per cent of phosphorus greatly increases its elastic modulus, as shown in Fig. 9. The process appears to be analogous to the

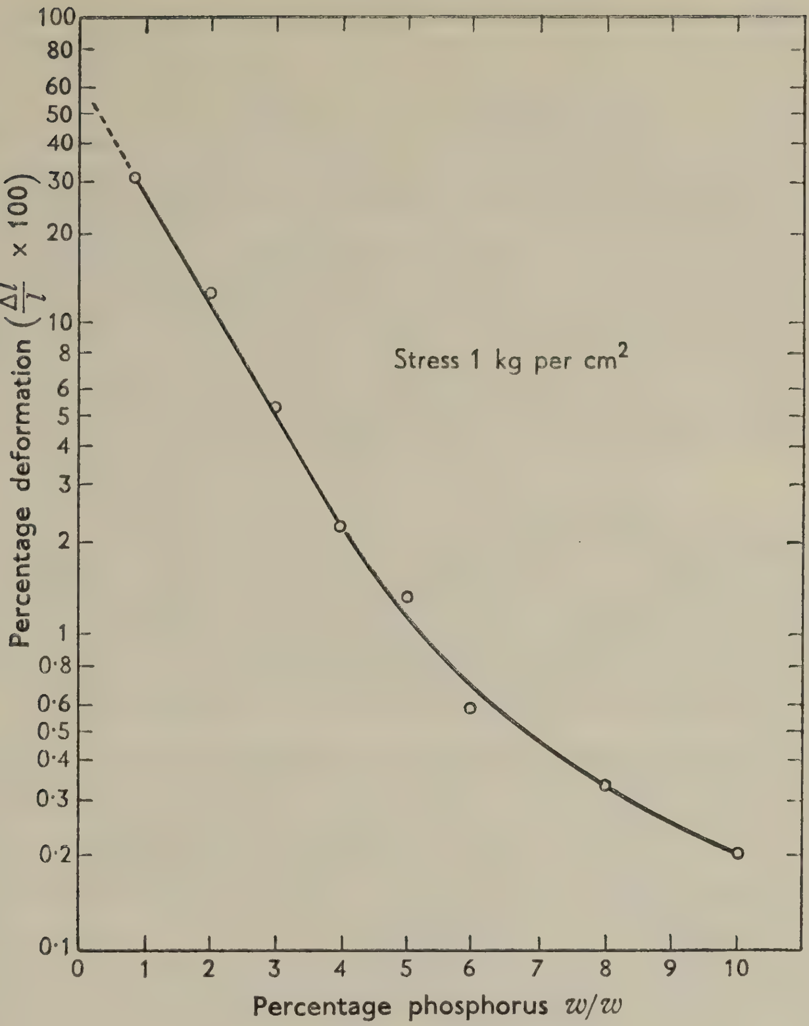


FIG. 9.—The effect of phosphorus on the elastic deformation of $\mu$ sulphur

vulcanization of natural rubber by sulphur, involving the progressive cross-linking of long polymer chains.[84] At low phosphorus contents ($< 5\%$) the variation of elastic deformation with temperature is typical of an elastomer, while when the composition approaches 10% P, the structure becomes highly cross-linked, and essentially vitreous.[85]

## COMMERCIAL APPLICATIONS OF PHOSPHORUS SULPHIDES

Commercial applications of the phosphorus sulphides have been reviewed.[41, 86] The chief outlet for tetraphosphorus trisulphide is still in the manufacture of matches (cf. Mellor, VIII, 1058), though it has been suggested as a heat transfer fluid because of its compatibility with stainless steel.[101] Nevertheless this sulphide has been surpassed in importance by tetraphosphorus decasulphide (phosphorus pentasulphide), which in the form of its organic derivatives is widely employed in the manufacture of lubricant additives of all kinds. The complex patent literature has been reviewed.[65, 87–8] It is mainly concerned with two classes of compounds:

(1) Metal salts of the organic phosphorodithioates formed by the reaction of alcohols or phenols with phosphorus pentasulphide.
(2) The reaction products of phosphorus pentasulphide with unsaturated organic compounds (polyolefines, terpenes, etc.).

These materials, and their decomposition products, adhere to metal bearing surfaces, so that oils which contain them, besides having good lubricating properties under extreme pressures, may inhibit corrosion of certain alloy metals.[89] Similar products act as antioxidants, and impart detergent properties to the base lubricant. Greases[90] and cutting oils containing such additives have also been described. The effect of additive structure on lubricant properties has been discussed.[91]

Many organophosphorus insecticides are based on phosphorus pentasulphide. The dialkyl phosphorodithioates can be converted directly into the phosphorodithioate insecticides such as malathion, while on chlorination they yield the dialkyl phosphorochloridothionates used in the manufacture of phosphorothioate insecticides like parathion, systox or diazinon.[92] Dicresyl phosphorodithioate and the sodium or ammonium salts of certain dialkylphosphorodithioic acids (especially the ethyl, *iso*propyl and *sec.*-butyl derivatives), are widely used in the flotation of sulphide minerals, where they function as 'collectors' in the same way as the alkyl xanthates.[86, 93] Other derivatives have been recommended as catalysts for the blowing of asphalts[94] and as antioxidants or colour improvers in rubber[95] and polyethylene.[96]

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### SECTION XII

# PHOSPHORUS OXYSULPHIDES

BY A. F. CHILDS

## General

Diphosphorus dioxytrisulphide, $P_2O_2S_3$, reported by Besson (Mellor, VIII, 1061) to result from the action of hydrogen sulphide on phosphoryl chloride, has not been subsequently investigated, although a substance of this composition is said to be formed by the action of hexamethyldisilthiane on phosphoryl chloride.[11] Tetraphosphorus hexaoxytetrasulphide, $P_4O_6S_4$, is now well authenticated, however, and two other oxysulphides have been reported. Tetraphosphorus tetraoxytrisulphide, $P_4O_4S_3$, is made by the action of oxygen on tetraphosphorus trisulphide. Although its formula suggests a formal analogy to tetraphosphorus heptasulphide, nothing certain is known of its structure. The nature of hexaphosphorus decaoxide pentasulphide, prepared by distillation of $P_4O_6S_4$ with excess of phosphorus pentoxide, is equally obscure.

## TETRAPHOSPHORUS TETRAOXYTRISULPHIDE, $P_4O_4S_3$

### PREPARATION

Solutions of tetraphosphorus trisulphide in benzene, carbon disulphide, carbon tetrachloride[1] or *o*-dichlorobenzene[2] react rapidly with dry air or oxygen with the formation of a voluminous precipitate. Analysis of the solvent-free material[1] as well as consideration of the quantity of oxygen absorbed[2] has established the empirical formula as $P_4O_4S_3$.

### PROPERTIES

Tetraphosphorus tetraoxytrisulphide is a fluffy, yellowish-white, apparently amorphous powder, insoluble in the usual solvents, and has a density of 1·96 at room temperature. On heating it softens at 150°C. and melts at 250°C. to a yellow liquid containing a suspended white solid. Sublimation *in vacuo* at 400°C. yields a volatile portion, which probably contains $P_4S_3$ and $P_4O_6S_4$, and leaves a residue (about 10% by weight of the original) which is decomposed by water with evolution of phosphine and hydrogen sulphide.

Phosphorus tetraoxytrisulphide deliquesces rapidly in the air, and inflames if moistened with a little water. When added carefully to a large volume of water it dissolves, giving a milky suspension of sulphur and a yellow residue of indeterminate composition. It reacts rapidly with aqueous sodium hydroxide forming a yellowish solution, which is decolorized on heating with evolution of phosphine and hydrogen.[1]

The only organic reaction of this oxysulphide described is that with olefins to give polymeric products of the empirical formula $(C_nH_{2n})_3,P_4S_3O_4$. These substances react further with alcohols or phenols[2] yielding polymeric esters which are claimed to have the formula $(C_nH_{2n})_3,P_4S_3O_4.(OX)_3$.

## TETRAPHOSPHORUS HEXAOXYTETRASULPHIDE, $P_4O_6S_4$

### PREPARATION

The formation of this substance by the interaction of tetraphosphorus hexaoxide and sulphur (Mellor, VIII, 1061) has been confirmed.[3, 4] The reaction is violent, and should be carried out only on a small scale to avoid the danger of an explosion. An alternative method is to heat a suitable mixture of phosphorus pentoxide and tetraphosphorus decasulphide, when the oxysulphide is formed according to the equation:

$$3P_4O_{10}+2P_4S_{10} \rightarrow 5P_4O_6S_4$$

If the reaction is carried out at 400–500°C. the oxysulphide distils off and condenses as a clear pale yellow liquid which rapidly solidifies. Redistillation under reduced pressure gives a purer product, which nevertheless has been claimed[9] to be less pure than that made by the original procedure. However, if the paste-like reaction product

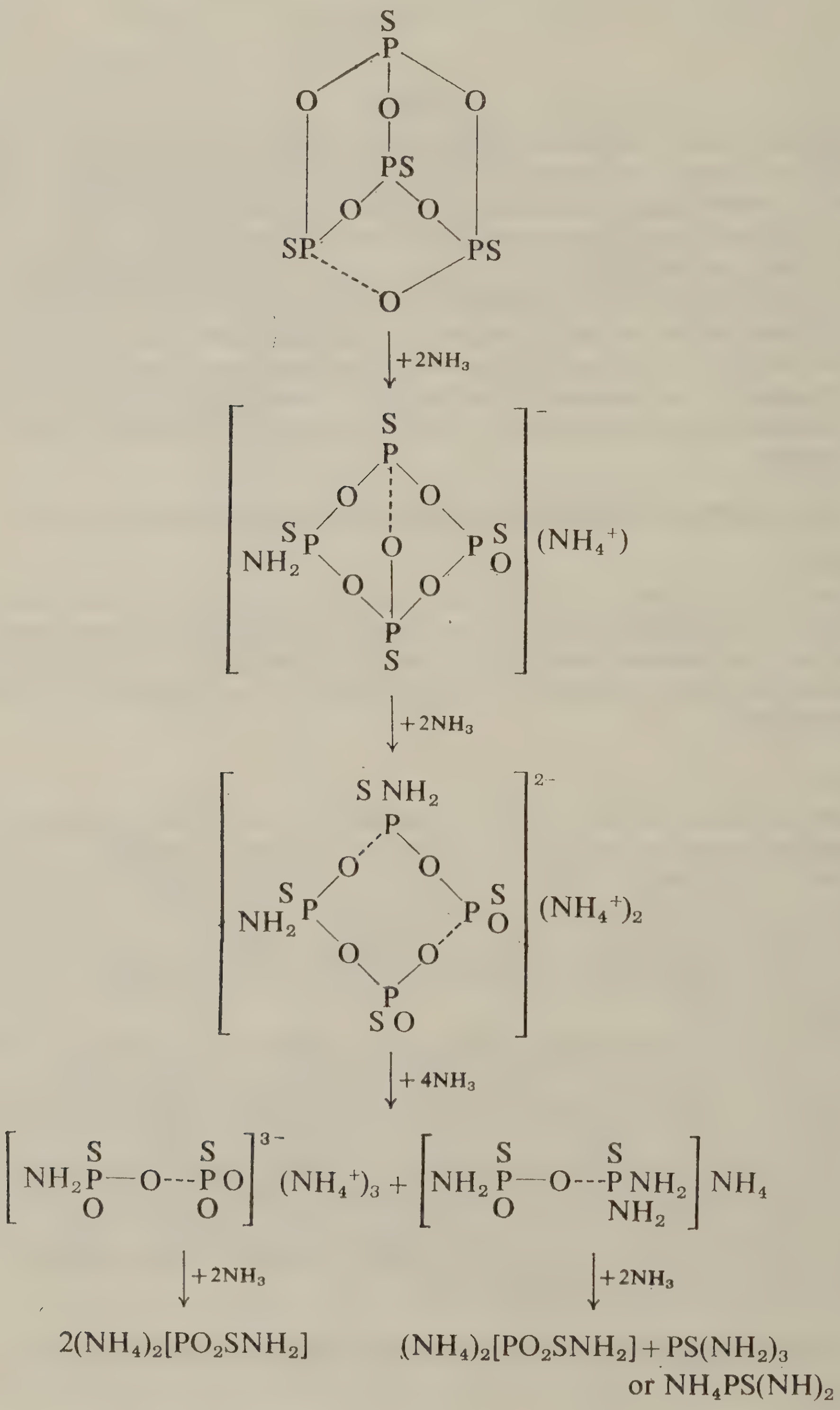

FIG. 1.—The ammonolysis of phosphorus hexaoxytetrasulphide

of sulphur and tetraphosphorus hexaoxide (m.p. 102°C.) is kept at 110°C., the initially yellow liquid becomes colourless, and large crystals of pure $P_4O_6S_4$ appear. On cooling to room temperature part of the substance remains a viscous liquid.[12]

Phosphorus tetraoxytrisulphide is also said to be formed by the action of air on molten phosphorus decasulphide,[5] but this reaction has apparently not been used as a preparative method.

### PHYSICAL PROPERTIES

Tetraphosphorus hexaoxytetrasulphide forms colourless deliquescent tetragonal plates, which decompose rapidly in moist air, and melt somewhat above 110°C.,[12] having b.p. 295°C./atm. pressure, 180–190°C./20 mm. Hg. The structure of the molecule has been determined by electron diffraction[3] and *X*-ray diffraction[12] and shown to be similar to that of phosphoric oxide, $P_4O_{10}$ (see page 389). The four phosphorus atoms are arranged tetrahedrally, oxygen atoms occupying the edges, and sulphur the apices of the tetrahedron. The bond angles are $O\text{–}P\text{–}O = 101{\cdot}5 \pm 1°$, $P\text{–}O\text{–}P = 123{\cdot}5 \pm 1°$, $O\text{–}P\text{–}S = 116{\cdot}5 \pm 1°$. As would be expected, the P–O bond distance of $1{\cdot}61 \pm 0{\cdot}02$ A. corresponds to a normal $\sigma$ bond with little $\pi$ bond character while the P–S bond ($1{\cdot}85 \pm 0{\cdot}02$ A.) exhibits considerable $\pi$ bond character.[6] The bond distances and angles found in the pure solid are closely similar.[12]

The Raman spectrum of phosphorus hexaoxytetrasulphide is broadly that which would be expected from a $P_4O_6S_4$ molecule of symmetry $T_d$, although extra polarized lines are exhibited which have been explained by a polymerization–depolymerization process occurring in the liquid. The appearance of solid particles during the irradiation supports this hypothesis.[7] A calculated value for the P═S bond distance, based on Raman data,[8] agrees exactly with that observed experimentally.[3]

### CHEMICAL PROPERTIES

Besides the reaction with water (Mellor, *loc. cit.*), only that with ammonia has been described.[9] The oxysulphide forms a clear colourless solution in liquid ammonia at −33°C., which slowly (more rapidly at room temperature) gives a sparingly soluble precipitate of diammonium phosphoramidothioate, $(NH_4)_2PO_2SNH_2$, and a solution in which infra-red spectroscopy shows the presence of thiophosphorylamide, $PS(NH_2)_3$, and an ammonium compound, presumably $NH_4PS(NH)_2$, since the white compound $[Ni(NH_3)_4][PS(NH)_2]_2$ can be precipitated. The proportion in which the products are formed is in accordance with the scheme (Fig. 1) based on the established structure of the oxysulphide.

## HEXAPHOSPHORUS DECAOXIDE PENTASULPHIDE, $P_6O_{10}S_5$

An oxysulphide of the above composition is obtained by distillation of tetraphosphorus hexaoxytetrasulphide with excess of phosphorus pentoxide. The hard white crystalline product can be purified by sublimation at 180°C. and 20 mm. Hg, forming white crystals, m.p. 122–125°C., which are hygroscopic and decomposed by water.[10] While nothing is known of its structure, the empirical formula would correspond to a mixed crystal, $P_4O_{10},5P_4O_6S_4$.

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## SECTION XIII

# FLUORIDES AND MIXED FLUORIDE HALIDES OF PHOSPHORUS

BY R. H. TOMLINSON

## PHOSPHORUS(III) FLUORIDE, PHOSPHORUS(III) CHLORO-, BROMO- AND IODO-FLUORIDES

### Preparation

Mixtures of phosphorus pentoxide with simple inorganic chlorides or fluorides at 500°C. give phosphoryl halides ($POX_3$) as the major volatile products. With calcium fluoride and sodium chloride together, mixed phosphoryl halides ($POCl_3$, $POCl_2F$, $POClF_2$, $POF_3$) are formed, while in iron reaction vessels or with heated carbon, some further reduction of phosphoryl fluoride to phosphorus(III) fluoride takes place.[1] Halogen exchange occurs when phosphorus(III) chloride or phosphoryl chloride is boiled under reflux with ammonium fluoride, and the main products are the mono- and trifluoro substituents.[2] Potassium fluoride in liquid sulphur dioxide is a convenient fluorinating agent for phosphorus trichloride and oxychlorides,[3] thus:

$$PCl_3 + 3KSO_2F = 3KCl + 3SO_2 + PF_3$$
$$POCl_3 + 3KSO_2F = 3KCl + 3SO_2 + POF_3$$

Addition of powdered antimony(III) fluoride to phosphorus(III) chloride containing antimony(V) chloride catalyst (Swarts' reaction[4]), or to phosphorus(III) bromide containing bromine as catalyst at temperatures above 15°C., gives largely phosphorus(III) fluoride. The threshold temperature of fluorination decreases with each fluorine atom introduced into the $PX_3$ molecule ($X =$ chlorine or bromine), but under precisely controlled conditions of temperature and pressure, such that the unfluorinated liquid halide remains at gentle reflux and the fluorinated product as it is formed distils out of the reaction zone, the reactions are shown to be stepwise, and major yields of the mixed trihalides $PX_2F$ and $PXF_2$ can be obtained.[5–7] Similar observations have been made on the reaction at reduced pressures between phosphorus(III) chloride or bromide vapour and heated calcium fluoride pellets. Mixed fluorochlorides were said to be formed in 50% yield by passing an equimolecular mixture of phosphorus(III) chloride and fluoride vapours through a glass tube packed with broken porcelain at 200°C.[8] Above 400°C. the equilibrium

$$PCl_3 + PF_3 \rightleftharpoons PF_2Cl + PFCl_2$$

shifts appreciably to the right, but side-products (notably $POF_3$ and $SiF_4$ from reactions with the glass) which are difficult to remove from $PF_2Cl$ by distillation, render the method unattractive for preparative purposes.[5] A less equivocal preparation is the action of hydrogen chloride upon dimethylaminophosphorus difluoride.[132] A similar method has been used to obtain phosphorus(III) difluoroiodide[132–3]:

$$Me_2NPF_2 + 2HX \rightarrow XPF_2 + Me_2NH,HX$$

Phosphorus(III) fluoride may be prepared by the dropwise addition, at 15°–40°C., of arsenic(III) fluoride containing antimony(V) chloride catalyst to phosphorus(III)

**Refs. p. 460**

chloride,[9] or of phosphorus(III) chloride to anhydrous zinc fluoride.[10–1] The vapours are led upwards through a column maintained at −80°C. and the product, obtained in approximately 85% yield, is condensed in a receiver cooled in liquid nitrogen. Good yields of phosphorus(III) fluoride have also been obtained by the reaction of phosphorus(III) chloride with disodium hexafluorosilicate,[134] or molten alkali metal fluoride mixtures,[135] and by the interaction of triphenyl phosphite and benzoyl fluoride.[136]

### Physical Properties

Gaseous phosphorus(III) fluoride is colourless when pure, and is only slowly hydrolyzed by moist air. It is odourless in toxic concentrations, producing chest pains, a sharp rise in body temperature and vomiting.[5]

Phosphorus(III) chloro- and bromo-fluorides are colourless in both gaseous and liquid states and form white solids on freezing. The liquid bromofluorides are unstable and decompose slowly at 'dry ice' temperatures to phosphorus(III) fluoride and bromide.[5] Phosphorus(III) difluoroiodide also disproportionates slowly in the vapour state, to phosphorus(III) fluoride and iodide, especially at pressures near atmospheric.[133]

Melting, boiling, vapour pressure and critical data are summarized in Table I.

Electron diffraction measurements[16–7, 164] confirm a pyramidal structure for the $PX_3$ halides in which the P-atom exhibits $p^3$ bonding and a tendency towards $sp^3$ hybridization with the non-bonding pair of $s$ electrons. Measurements on pure rotational transitions in the microwave region[18–21] have permitted precise estimates to be made of intermolecular distances and of dipole moment for phosphorus trifluoride as shown in Table II. Microwave data have also been used to deduce first order centrifugal distortion constants for phosphorus trifluoride and trichloride.[137]

The infra-red spectra for phosphorus(III), phosphorus(V) and phosphoryl fluoride have been obtained.[27] Correlation with the available Raman and structural data permits an assignment of the fundamental frequencies and an evaluation of the force constants for the $PF_3$ and $POF_3$ molecules (Tables III and XI, respectively) using Wilson's method of matrices. A later author[28] has, however, obtained quite different values for $PF_3$. The infra-red and nuclear magnetic resonance spectra of phosphorus(III) chlorodifluoride[138] and difluoroiodide[133] have been recorded.

Values of potential constants based on the Urey and Bradley force field using the earlier frequency assignments[29] have been reported as follows (values in $10^5$ dynes cm.$^{-1}$):

| | $K$ | $H$ | $F$ | $F'$ |
|---|---|---|---|---|
| $PF_3$ | 3·910 | 0·296 | 0·935 | −0·813 |
| $PCl_3$ | 1·680 | −2·212 | 0·743 | −0·420 |
| $PBr_3$ | 1·436 | −0·142 | 0·522 | −0·313 |
| $PI_3$ | 1·031 | −0·080 | 0·338 | −0·214 |

The negative values of $F'$ indicate repulsive forces between the non-bonding atoms.[30]

The heat of formation $\Delta H^\circ_{f_{25}}$ for phosphorus(III) fluoride gas is given as −189 kcal./mole,[31] or as −221·95 kcal./mole with P($\omega$, $\beta$, 0°K.) as standard state.[32] A later value of $\Delta H^\circ_{f_{25}}$ of −226·03 kcal./mole has been derived from the heat of reaction between calcium fluoride and phosphorus trichloride in a fluidized bed,[139] and combined with other values of spectroscopic data to give values of the standard free energy and entropy of formation, $\Delta G^\circ_{25} = -242{\cdot}36$ kcal./mole, $S_0 = 54{\cdot}78$ e.u./mole. The data support a linear relationship of P–X bond energy with P–X bond length for the series of phosphorus(III) halides.[140] Enthalpy, free energy and entropy functions at 100° intervals from 298·1 to 1000°K., have been derived[31, 33–4] from molecular data,[22] and a more recent computation[32] gives free energy, entropy and heat capacity at similar temperature intervals up to 5000°K. A selection of these data is made in Table IV. Similar functions are derived[35] for the mixed trihalide $PFCl_2$ between 100° and 1000°K.

Table I.—Physical Properties of the Phosphorus(III) Halides

| Compound | Reference | m.p. °C. | b.p. °C. | Vapour pressure (mm.) | | | Heat of vaporization kcal. | Trouton's constant | Critical temp. °C. | Critical pressure atm. | Density at 0°C. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $\log_{10} p = B - A/T$ | | range °K. | | | | | |
| | | | | $A$ | $B$ | | | | | | |
| $PF_3$ | 5 | −151·5 | −101·15 | 761·4 | 7·310 | 122–183 | 3·49 | 20·3 | 2·05 | 42·7 | — |
| | 1 | −151·5 | −101·8 | 861·9 | 7·927 | 122–183 | 3·95 | 23·1 | — | — | — |
| $PF_2Cl$ | 5 | −164·8 | −47·3 | 939·7 | 7·043 | 190–231 | 4·20 | 19·1 | 89·17 | 44·6 | — |
| $PFCl_2$ | 2 | −144·2 | 13·85 | 1308 | 7·439 | 228–291 | 5·95 | 20·7 | 189·84 | 49·3 | — |
| $PCl_3$ | 12–14 | −93·6 | 75·2 | 1653·6 | 7·6285 | 288–348 | 7·57 | 21·7 | 285·5 | — | 1·6128 |
| $PF_2Br$ | 5 | −133·8 | −16·1 | 1217·9 | 7·620 | 222–258 | 5·72 | 22·3 | 113 | — | — |
| $PFBr_2$ | 5 | −115 | 78·4 | 1646·2 | 7·866 | 296–351 | 7·62 | 21·7 | 254 | — | 2·1810 |
| $PBr_3$ | 13–15 | −40·5 | 173·3 | 2061 | 7·498 | 343–458 | 9·42 | 21·1 | — | — | 2·9231 |
| $PF_2I$ | 133 | −93·8 to −93·3 | 26·7 (extrap.) | 1514 | 7·929 | | — | 23·09 | | | |

*Table II.—Molecular Data for the Phosphorus(III) Halides*

| Compound | Reference | Bond length, A. | | Bond angle ° | | Dipole moment (debye units) |
|---|---|---|---|---|---|---|
| $PF_3$ | 18 | P–F | 1·546 ± 0·008 | FPF | 104 ± 3 (assumed) | |
| | 164 | P–F | 1·537 ± 0·004 | FPF | 98·2 ± 0·6 | |
| | 19 | | | | | 1·025 ± 0·009 |
| | 21 | | | | | 1·03 ± 0·01 |
| $PFCl_2$ | 16 | P–F | 1·55 ± 0·04 | FPCl | 102 ± 3 | |
| | | P–Cl | 2·02 ± 0·03 | | | |
| $PCl_3$ | 22 | P–Cl | 2·00 ± 0·02 | ClPCl | 101 ± 2 | (0·9, ref. 30, 31) |
| | 23 | P–Cl | 2·043 ± 0·003 | ClPCl | 100·1 ± 0·33 | |
| $PBr_3$ | 24 | P–Br | 2·23 ± 0·01 | BrPBr | 100 ± 2 | (0·6, ref. 30, 31) |
| | 25 | P–Br | 2·18 ± 0·03 | BrPBr | 101·5 ± 1·5 | |
| $PI_3$ | 24 | P–I | 2·52 ± 0·01 | IPI | 98 ± 4 | (0·34, ref. 26) |
| | 25 | P–I | 2·43 ± 0·04 | IPI | 102 ± 2 | |

*Table III.—Force Constants* ($10^5$ *dynes cm.*$^{-1}$) *for the Phosphorus(III) Halides*

| Compound | Reference | $f_d$ | $f_{dd}$ | $f_\alpha$ | $f_{\alpha\alpha}$ | $f_{d\alpha}$ |
|---|---|---|---|---|---|---|
| $PF_3$ | 27 | 4·64 | 0·78 | 1·15 | −0·09 | — |
| | 29 | 4·5900 | 0·3823 | 1·005 | 0·1815 | −0·1191 |
| | 28 | 5·02 | 0·352 | 0·632 | 0·145 | — |
| $PCl_3$ | 29 | 2·1200 | 0·2591 | 0·2840 | 0·0710 | 0·0116 |
| | 28 | 2·13 | 0·193 | 0·311 | 0·060 | — |
| $PBr_3$ | 29 | 1·6300 | 0·1244 | 0·1995 | 0·0723 | 0·0307 |

*Table IV.—Thermodynamic Properties of* $PF_3(g)$ *in Ideal Gas State*

| Temperature °K. | $-\frac{G^\circ - H^\circ_0}{T}$ g.-cal. mole$^{-1}$ deg.$^{-1}$ | $H^\circ - H^\circ_0$ g.-cal. mole$^{-1}$ | $S^\circ$ g.-cal. mole$^{-1}$ deg.$^{-1}$ | $C^\circ_p$ g.-cal. mole$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|---|
| 273·1 | 53·887 | 2,748 | 63·947 | 13·479 |
| 298·1 | 54·782 | 3,092 | 65·153 | 14·028 |
| 300 | 54·846 | 3,118 | 65·240 | 14·067 |
| 400 | 57·998 | 4,617 | 69·540 | 15·792 |
| 500 | 60·681 | 6,257 | 73·195 | 16·929 |
| 600 | 63·036 | 7,990 | 76·352 | 17·679 |
| 700 | 65·140 | 9,785 | 79·118 | 18·188 |
| 800 | 67·043 | 11,622 | 81·571 | 18·544 |
| 900 | 68·782 | 13,489 | 83·770 | 18·800 |
| 1000 | 70·382 | 15,380 | 85·762 | 18·991 |
| 1100 | 71·864 | 17,287 | 87·579 | 19·136 |
| 1200 | 73·244 | 19,206 | 89·249 | 19·248 |
| 1300 | 74·535 | 21,137 | 90·794 | 19·337 |
| 1400 | 75·749 | 23,072 | 92·229 | 19·408 |
| 1500 | 76·892 | 25,017 | 93·570 | 19·466 |
| 2000 | 81·798 | 34,800 | 99·198 | 19·641 |
| 2500 | 85·733 | 44,643 | 103·590 | 19·723 |
| 3000 | 89·018 | 54,119 | 107·191 | 19·769 |
| 4000 | 94·307 | 74,312 | 112·885 | 19·814 |
| 5000 | 98·481 | 94,140 | 117·309 | 19·835 |

The difference between calculated and experimental molar entropy values for phosphorus(III) fluoride and phosphoryl chloride termed 'entropy of resonance', was 4·5 and 6·7 g.-cal. deg.$^{-1}$ mole$^{-1}$, respectively[36]; the empirical formula used in the calculation involved the Sackur–Lewis and Eastman formulae[37] as special cases.

Three solid forms of phosphorus(III) fluoride (III, II and I) have been reported, with the following thermodynamic properties[141]:

| Transition | $\Delta H$ g.-cal./mole | $S°$ e.u. | $T$°K. |
|---|---|---|---|
| III → II | 59·9 | 0·715 | 83·75 |
| II → I | 552·3 | 4·995 | 110·56 |

Heat capacity values for phosphorus(III) fluoride gas in the temperature range 298·1 to 1000°K. are given[38] by $C_p = 17{\cdot}559 + 0{\cdot}001972T - 456{,}900/T^2$ g.-cal. mole$^{-1}$; heat capacity, viscosity and thermal conductivity data at 100° intervals between 100° and 5000°K. for phosphorus(III) fluoride, phosphorus(III) chloride gases and for the PF radical have been obtained[39]; the specific conductance of liquid form phosphorus(III) fluoride[40] at −113°C. is $0{\cdot}42 \times 10^{-9}$ mho cm.$^{-1}$

## Chemical Properties

Addition of chlorine to phosphorus(III) fluoride gives dichlorofluorophosphorane (see page 451), b.p. 7·1°C.[41] The reaction is catalyzed by glass surfaces,[42] which suffer rapid attack in contact with the liquid product.[5] Phosphorus(III) chlorofluorides take up chlorine in the presence of iodine as catalyst to give unstable liquid products which decompose to phosphorus(V) fluoride and chloride at room temperature. Coloured unstable liquid products thought to be $PBr_4F$ and $PBr_3F_2$ were reported to arise from the interaction of phosphorus(III) bromofluorides and bromine, but were not further characterized.[5]

Reorganization in liquid phosphorus(III) halide mixtures is confirmed both by Raman and by nuclear magnetic resonance studies. Thus, Raman spectra have shown the presence of phosphorus(III) chlorobromides, chloroiodides, bromoiodides and fluorochlorobromide in phosphorus(III) chloride–bromide,[43] chloride–iodide,[44] bromide–iodide[45] and dichlorofluoride–dibromofluoride[46–7] mixtures, respectively. For each of the systems $P(OC_6H_5)_3$–$PCl_3$, $P(OC_6H_5)_3$–$PBr_3$ at 180°C. and $PCl_3$–$PBr_3$ at 25°C., as well as for equimolar mixtures of $P(OC_6H_5)_3$,$PCl_3$ and $PBr_3$ at 180°C., nuclear magnetic resonance measurements at equilibrium showed larger amounts of the possible mixed phosphorus(III) compounds (except for $PClBr_2$) than would correspond to completely random reorganization.[48] For the system $PCl_3$–$PBr_3$ at 25°C., mixed compounds were detected within 15 min. of mixing and equilibrium concentrations were present after 1 week. Attainment of equilibrium in such triply connected systems is considerably faster than in the phosphoryl halide systems containing the same ligands[48]; the presence of fluoride reduces the rate of the reaction.[49]

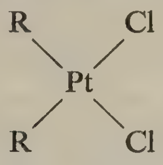
Thermal analysis of the phosphorus trifluoride–boron trifluoride system showed a single eutectic at −163·5°C. (21·5 mole % $BF_3$) and no evidence of compound formation.[50] In contrast, if boron trifluoride is passed through a petroleum ether solution of *n*-propylphosphine, $PPr_3$, the solid complex $PPr_3$,$BF_3$ is immediately precipitated.[51] With diborane under 8 atm. pressure, unstable phosphorus trifluoride–borane is formed as a colourless gas, spontaneously inflammable in air and analogous to carbon monoxide–borane[52]:

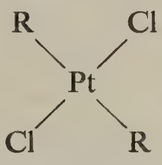
| | $PF_3$,$BH_3$ | CO,$BH_3$ |
|---|---|---|
| M.p. °C. | −116·1 | −137·0 |
| B.p. °C. | −61·8 | −64 |
| Latent heat of vaporization (g.-cal.mole$^{-1}$) | 4760 | 4750 |
| Trouton's constant | 22 | 23 |
| Dissociation constant (atm.) at 25°C. | 1·0 ± 0·3 | 2·5 |
| % decomposed in 1 hr. at 25°C. | 14 | 17 |

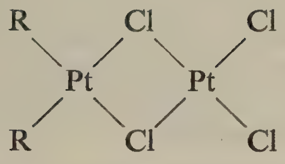
Pentaborane reacts analogously to diborane, giving a mixture of the borane and tetraborane adducts[142]:

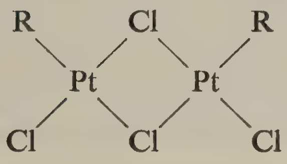
$$B_5H_{11} + 2PF_3 \rightarrow BH_3,PF_3 + B_4H_8,PF_3$$

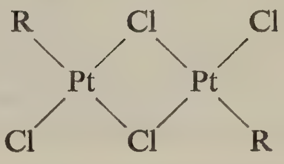
Phosphorus(III) fluoride reacts with platinous chloride at −200°C. to form a mixed sublimate which, when further sublimed in the presence of phosphorus(III) fluoride, gives white crystals of bis(trifluorophosphine)dichloroplatinum, $(PF_3)_2PtCl_2$; this 'dichloride' has m.p. 102°C. Alternatively, if the sublimate is refluxed with platinous chloride in a nitrogen atmosphere at 100 mm. pressure and further resublimed at 15 mm. it gives orange-red crystals of dichlorobis(trifluorophosphine)$\mu\mu'$-dichlorodiplatinum, $(PF_3)_2Pt_2Cl_4$; this 'tetrachloride' has m.p. 155° to 156°C.[10] Boiling points (with rapid decomposition) of the di- and tetrachlorides are 240° and 290°C., respectively, and both chlorides are rapidly hydrolyzed by water. Planar square configuration about the platinum nucleus corresponding to *dsp*$^2$ bonding is established for $PtCl_2R_2$ and $(PtCl_2R)_2$ type compounds,[53–4] the former with two and the latter with three possible *cis-trans* isomerides thus:


*cis*


*trans*


*cis*


*trans unsym.*


*trans sym.*

The 'dichlorides' with R = $PF_3$ or CO are considered from their solubilities in inert solvents and from dipole measurements to have a mainly *cis*-configuration in solution. Substitution of X = fluorine atoms for alkyl groups in such complexes where R = $PX_3$, greatly increases the stability of the *cis*-isomer relative to the *trans*.[10] The reaction of platinous chloride with phosphorus(III) fluoride in the presence of copper powder at 100°C. and 100 atm. yields the completely substituted compound $Pt(PF_3)_4$, m.p. −15°C., b.p. 86°/730 mm. $Pd(PF_3)_4$, a white solid m.p. −41°C., decomp. −20°C., can be made in similar fashion[143] or from $Pd(CO)_2Cl_2$ and phosphorus(III) fluoride under pressure.[144] However the copper catalyzed reaction of rhodium trichloride, hydrogen and phosphorus(III) fluoride gives $HRh(PF_3)_4$, a clear mobile liquid with an irritating odour, m.p. −40°C., b.p. 89°/125 mm.[145]

Phosphorus trifluoride forms black, hygroscopic addition compounds with ruthenium or osmium tetroxides:

$$RuO_4 \xrightarrow[-100°C.]{} (RuO_4)_2,PF_3 \xrightarrow[+20°C.]{} RuO_4,PF_3$$
$$OsO_4 \xrightarrow[-100°C.]{} (OsO_4)_2,PF_3 \xrightarrow[+70°C.]{} OsO_4,PF_3$$

Neither product has a stability approaching that of the complexes with platinous chloride and it is reasonable to suppose that similar bonding does not occur.[61] Both phosphorus trichloride and tribromide reduce the tetroxides to give 1:1 addition compounds of the type $RuO_2,PCl_3$.

Phosphorus trifluoride fails to react with finely divided nickel at 150 atm. and 200°C.,[55] but yields $Ni(PF_3)_4$ at 300 atm. and 100°C.[146] It also reacts with nickel tetracarbonyl in the presence of metallic nickel to give a random mixture of compounds of the general formula $Ni(CO)_x(PF_3)_{4-x}$, from which pure compounds may be separated by gas–liquid chromatography.[147] However, substitution of carbonyl in nickel carbonyl with phosphorus trichloride readily goes to completion in the liquid phase, and excess trichloride can be removed by distillation. From the residue pale yellow crystals of tetrakistrichlorophosphine nickel, $Ni(PCl_3)_4$, can be obtained by recrystallization from pentane. Further treatment of the chloro-compound with phosphorus trifluoride at 50 to 100 atm. and 100°C. or with phosphorus tribromide at 70°C. gives 50 to 60% conversion to the fully substituted fluoro- and bromo-compounds respectively. The fluoride reaction has been shown to involve exchange of $PF_3$ for $PCl_3$ and not halogen interchange.[148] The stabilities of the tetrakistrihalogenophosphine nickel compounds decrease in the order fluoride > chloride > bromide. The fluoride is a colourless, odourless, volatile liquid, m.p. $-55°$, b.p. 70·7°C., insoluble in water and volatile in steam with little hydrolysis; the chloride and bromide are thermochromic crystalline solids, decomposing above 80°C.[55] The chloride has been shown to yield phosphorus(III) chloride, nickel(II) chloride, heptanickel triphosphide and dinickel phosphide on decomposition.[148] The chloride is diamagnetic[55] like nickel carbonyl, which was shown by *X*-ray analysis[56] to be tetrahedral. It seems probable that the tetrakistrihalogenophosphine nickel compounds and nickel carbonyl have a similar structure.[55, 57] Interest in these compounds arose from consideration of the nature of the co-ordinate linkage with $C_2H_4$, CO and $PF_3$ type ligands, the boron trifluoride and boron hydride complexes of which are either nonexistent or very unstable, but the platinous chloride complexes are stable to 180°–300°C. Such ligands are *trans*-directing in the latter compounds and contrast with *cis*-directing ligands, such as ammonia and primary amines, which form stable boron complexes containing the classical coordinate link.[51] The failure of phosphorus(III) fluoride to form a boron trifluoride complex implies[58] that the lone pair on the phosphorus atom is withheld from $\sigma$-bond formation; with phosphorus(III) chloride, unstable $PCl_3,BF_3$ was reported to be formed[57] (but see page 475) in agreement with the more electropositive character of the chlorine atom compared with fluorine. Co-ordination with platinum is explained on the assumptions that:

(i) $\pi$ bonding occurs by overlap of a platinum 5*d*-electron pair with a vacant 3*d*-orbital of the P-atom,
(ii) acceptance of electrons by the P-atom makes its 3*s* electrons more readily available for the $\sigma$-bond.

The large inductive effect of the fluorine atoms enhances such $\pi$-bonding, but in the general case of $PX_3$ complexes, decrease in the electronegativity of X (= halogen) decreases electron drift from available *d*-orbitals of the metal to the P-atom.[51, 58] Support for the double bond character of the metal ligand bond in these complexes is suggested by analogy with the *o*-phenylenebisdimethyl arsine and 2:2′-dipyridyl nickel carbonyl disubstituted complexes, where comparison of bond length and stretching force constants for the carbonyl bond indicated considerable double bond character for the Ni–As and Ni–N bonds, respectively.[59] Tetrakistrifluorophosphine nickel and related compounds, viz:

| | | | | |
|---|---|---|---|---|
| $Ni(PF_3)_4$ | m.p. $-55°$C. | b.p.$_{(760\text{ mm.})}$ | 70·5°C. | (20–35% yield) |
| $Ni(PF_2CH_3)_4$ | — | b.p.$_{(3\text{–}4\text{ mm.})}$ | 66–68°C. | (unstable) |
| $Ni(PF_2C_6H_5)_4$ | m.p. 63·5°C. | — | | (stable) |

have been obtained[60] by fluorination of the chloro-analogues with potassium fluorosulphinate in benzene or dichlorobenzene solution. With liquid ammonia, polymeric nickel tetrakis-nitridophosphine is formed:

$$Ni(PF_3)_4 \xrightarrow[NH_3(l)]{} Ni[P(NH_2)_3]_4 \xrightarrow[\text{of } NH_3]{\text{evaporation}} [Ni(PN)_4]_x$$

Iron pentacarbonyl reacts with phosphorus(III) fluoride at high temperatures and pressures yielding the series of compounds of general formula $Fe(CO)_{5-x}(PF_3)_x$ ($x = 1$–5). All are yellow liquids except pentakis-(trifluorophosphine)-iron(0), which is a yellow solid, m.p. 44°C.[149] The same material can also be made by the copper catalyzed reaction of phosphorus(III) fluoride and iron(II) iodide at 140°C. and

500 atm. It is diamagnetic, soluble in the common organic solvents and fairly stable in moist air. Potassium amalgam converts it to potassium trifluorophosphine-ferrate.[150]

Iron nitrosyl bromide, $[Fe(NO)_2Br]_2$, reacts with phosphorus(III) fluoride to give bis-(trifluorophosphine)-dinitrosyl iron(I), $Fe(NO)_2(PF_3)_2$. The analogous tris-(trifluorophosphine)-nitrosyl cobalt, $Co(NO)(PF_3)_3$ is obtained from $[Co(NO)_2Cl]_2$ and $PF_3$. It is a reddish-brown mobile liquid, m.p. −92°C., b.p. 81°/732 mm., decomp. 163°, fairly stable in moist air.[151]

Dicobalt octacarbonyl reacts with phosphorus(III) fluoride under pressure in the presence of hydrogen or hydrogen fluoride forming pale yellow tris-(trifluorophosphine)-carbonyl cobalt hydride, $HCo(PF_3)_3CO$, m.p. −67°, b.p. 80·5°/715 mm. This compound is only slowly decomposed by air, and in aqueous solution behaves as a strong monobasic acid. With potassium amalgam it yields crystalline potassium tris-(trifluorophosphine)-carbonyl cobaltate $K[Co(PF_3)_3CO]$.[152] The analogous tetrakis(trifluorophosphine) cobalt hydride, $HCo(PF_3)_4$, is obtained by the copper catalyzed reaction of cobalt(II) iodide and phosphorus(III) fluoride at 200°C. and 250 atm. It is a greenish mobile liquid, m.p. −51°C., b.p. 80°/730 mm., quite stable in air, but decomposing when heated to 250°C. Again, it is a strong monobasic acid, and with potassium amalgam yields potassium tetrakis(trifluorophosphine)-cobaltate, $K[Co(PF_3)_4]$.[153]

Hexakis (trifluorophosphine)-chromium(0), $M(PF_3)_6$, can be made by treating dibenzene-chromium(0) with phosphorus(III) fluoride. It forms colourless highly refractive prisms, m.p. 193°C., decomp. 300°C., stable in dry air and soluble in polar organic solvents.[154] The analogous molybdenum compound, m.p. 196°C., decomp. 250°C., is made in similar fashion,[155] while hexakis (trifluorophosphine)-tungsten(0), m.p. 214°C., decomp. 320°C., is obtained by treating tungsten(VI) chloride with phosphorus(III) fluoride in the presence of copper at 200°C. and 200 atm.[153] All three compounds are diamagnetic, and their infra-red spectra suggest an octahedral structure.

Mixed carbonyl-trifluorophosphine derivatives of chromium and molybdenum have been made by treating the metal hexacarbonyl, triammine tricarbonyl or mesitylene tricarbonyl with phosphorus(III) fluoride. Tris-(trifluorophosphine)-tricarbonyl molybdenum(0) (m.p. 89°C., decomp. 110°)[155] and the chromium analogue (m.p. 68°C.)[154] have been isolated as colourless highly refractive solids.

A 1:1 mixture of phosphorus trifluoride with oxygen at −75° to −60°C. in the silent electric discharge is partially converted to phosphoryl fluoride, phosphorus pentafluoride, pyrophosphoryl fluoride ($P_2O_3F_4$, m.p. −0·1°C., b.p. 75°C.) and polymeric phosphorus dioxyfluoride $(PO_2F)_n$[62] (see page 459).

Phosphorus trifluoride fails to combine with potassium fluoride on prolonged standing in a sealed tube; above 200°C. some disproportionation of the trifluoride in the mixture to phosphorus and phosphorus pentafluoride occurs.[40] Difluorodiazine, $N_2F_2$, however converts phosphorus trifluoride to phosphorus pentafluoride at room temperature.[156]

## Difluorophosphine, $F_2PH$

Following unsuccessful earlier attempts to make chloro- and bromo-phosphines,[157] difluorophosphine has been prepared in 55% yield by the reduction of phosphorus(III) difluoroiodide by hydrogen iodide in the presence of mercury at room temperature:

$$PF_2I + HI + 2Hg \rightarrow PHF_2 + Hg_2I_2$$

Hydrogen, phosphorus trifluoride and an unstable material, probably $PHF_2,HI$, were observed as by-products.

Difluorophosphine is a colourless gas stable at low pressures, and decomposing less than 5% in 5 hr. even at room temperature and saturation pressure. The formula is supported by hydrogen analysis, molecular weight (vapour density), mass spectrum, and the $^1H$ and $^{19}F$ nuclear magnetic resonance spectra.

Difluorophosphine is associated in the condensed phase but monomeric in the vapour. Its freezing point (−124·2 to −123·6°C.) and boiling point (−64·6°C. (extrap.)) are higher than those of either phosphine or phosphorus(III) fluoride. The vapour pressure is given by the equation:

$$\log p_{(\text{mm.})} = -1126/T + 8{\cdot}280$$

and the Trouton constant is 24·7 g.-cal. deg.$^{-1}$ mole$^{-1}$.

Under alkaline conditions difluorophosphine reduces water:

$$PHF_2 + H_2O \rightarrow PF_2OH + H_2$$

though the more usual reaction:

$$PHF_2 + 2H_2O \rightarrow HP(OH)_2 + 2HF$$

occurs to some extent.[158]

### Diphosphorus Tetrafluoride, $P_2F_4$

Fluorination of diphosphorus tetraiodide by antimony pentafluoride leads mainly to phosphorus trifluoride and pentafluoride, though a small amount of less volatile material of molecular weight approaching $P_2F_4$ is formed.[159] This substance can, however, be made in 85% yield by the reaction of phosphorus(III) difluoroiodide with mercury at room temperature:

$$2PF_2I + 2Hg \rightarrow P_2F_4 + Hg_2I_2$$

After purification by fractional condensation at −135°C., diphosphorus tetrafluoride is obtained as a colourless gas, m.p. −86·5°C., b.p. −6·2°C, Trouton constant 22·11 g.-cal./deg./mole and heat of vaporization 5·90 kcal./mole. The vapour pressure data follow the equation:

$$\log p_{(\text{mm.})} = -1290/T + 7{\cdot}716$$

The analysis, molecular weight (vapour density) and mass spectrum are all in agreement with the formula assigned. The infra-red spectrum of diphosphorus tetrafluoride shows absorptions at 842(s), 830(vs), 820(s), 408(vw) and 356(w) cm.$^{-1}$

A by-product formed in small yield during this preparation has been tentatively identified as diphosphorus oxytetrafluoride, $PF_2OPF_2$, by its molecular weight (vapour density), and infra-red and mass spectra. It may also be prepared directly in 67% yield by reaction between diphosphorus tetrafluoride and oxygen.[160]

## PHOSPHORUS(V) FLUORIDE

### Preparation

Almost theoretical yields of phosphorus(V) fluoride and corresponding metal fluoride are obtained from the thermal decomposition of sodium, calcium or barium hexafluorophosphates between 300° and 1000°C.[63] The action of acidic inorganic chlorides such as hydrogen chloride, phosphorus pentachloride, antimony(V) or ferric chlorides, on sodium hexafluorophosphate at 200–350°C. also yields phosphorus(V) fluoride.[161] Other procedures proposed in the patent literature include the reactions between phosphorus(III) fluoride, chlorine or bromine and calcium fluoride at 325° to 500°C.,[64] and between not less than 5:3 molar mixtures of phosphorus(III) fluoride and chlorine or bromine when passed through a tubular reactor (packed with 'Adsorbite') at 250° to 600°C.[65] Both reactions provide good yields of phosphorus(V) fluoride, but the conditions of the second patent processes afford continuous operation without deposition of solid pentahalides and consequent blocking of cooler parts of the line. Phosphorus(III) chloride and small amounts of mixed trihalide by-products are separated at −80°C. and are later returned to the process after halogen exchange with heated calcium fluoride. The preparation from arsenic trifluoride and phosphorus pentachloride (Thorpe, Mellor, VIII, 996) has been further described[66]; a copper reaction vessel was used. For the reaction between phosphorus(V) chloride vapour, in a nitrogen carrier stream, with calcium fluoride, 80 to 90% conversion to phosphorus pentafluoride is reported.[67] In all these processes strictly anhydrous conditions were found to be essential for efficient recoveries. Phosphorus pentafluoride also results from the fluorination of phosphorus pentachloride by sodium hexafluorosilicate[135] or difluorodiazine.[156]

### Physical Properties

The pure substance boils at −84·5°C., m.p. −93·7°C. Vapour pressures from −125·6° to −84·5°C. are represented by $\log_{10} p_{\mathrm{mm.}} = -A/T + B$ where $A = 1518{\cdot}8$ and $898{\cdot}8$, $B = 11{\cdot}101$ and $7{\cdot}646$ for the sublimation and vaporization curves respectively. The heats of sublimation, fusion and vaporization are 6940, 2830 and 4110 g.-cal. mole$^{-1}$ and Trouton's constant = 21·8. The dielectric constant is 1·002063, independent of temperature,[66] the refractive index (Na$_{\mathrm{D}}$, 760 mm.) is 1·0006416 and the derived electron and atom polarization values are 9·2 and 6·2, respectively.[68] The heat of formation was estimated, by extrapolation from available data for sodium, aluminium, silicon and sulphur fluorides, as −315 kcal./mole.[69] However, two direct determinations by combustion of white phosphorus in fluorine gave higher values, in excellent agreement, of $\Delta H^{\circ}_{f\,\mathrm{PF_5(g)}}$ at 25°C. = $-381{\cdot}4 \pm 0{\cdot}8$[162] and $-380{\cdot}8 \pm 0{\cdot}3$[163] kcal./mole. The latter authors also report values of high temperature thermodynamic functions for gaseous $\mathrm{PF_5}$.

In the vapour state phosphorus(V) halide molecules have trigonal bipyramidal structures approximating to $sp^3d$ hybridization at the P-atom. Early electron diffraction measurements[16, 70] appeared to indicate equal P–F distances of 1·57 ± 0·02 A. in phosphorus pentafluoride. Later determinations,[164–5] while differing from one another, agree in assigning a greater length to the axial than to the equatorial P–F bonds. The chlorine atoms in phosphorus dichlorotrifluoride were first thought to occupy axial positions with fluorine and phosphorus atoms coplanar,[16, 70] but subsequent infra-red and Raman data suggest that the chlorine atoms occupy equatorial positions.[166] Two P–Cl distances are also observed for phosphorus pentachloride in the gaseous state, corresponding to the axial and equatorial chlorine atoms respectively.[71] Raman methods[72–5] show all five P–Cl bonds alike at temperatures above the melting point, but in the solid state the molecule is unsymmetrical and ionic (see page 476). Bond lengths (A.) determined in the above work are:

| | | $\mathrm{PF_5}$ | | $\mathrm{PF_3Cl_2}$ | $\mathrm{PCl_5}$ |
|---|---|---|---|---|---|
| P–F | (axial) | 1·549 ± 0·005,[164] | 1·577[165] | | |
| | (equatorial) | 1·499 ± 0·005 | 1·534 | 1·59(±0·03) | |
| P–Cl | (axial) | | | 2·05(±0·03) | 2·19(±0·06) |
| | (equatorial) | | | | 2·04(±0·06) |

Some controversy on the detailed assignments of the fundamental vibrations in the infra-red spectrum of phosphorus pentafluoride[166] has now been resolved.[167–8] The vapour infra-red spectra and low temperature liquid Raman spectra of phosphorus pentafluoride and the fluorochlorophosphoranes are all consistent with trigonal bipyramidal structures.[27, 166] $\mathrm{PCl_4F}$ has a $C_{3v}$ structure with the fluorine occupying an axial position. In $\mathrm{PCl_3F_2}$ ($D_{3h}$) both fluorine atoms are axial, while in $\mathrm{PCl_2F_3}$($C_{2v}$) the fluorine atoms occupy one equatorial and two axial positions.[166] Nuclear quadruple resonance[180] and dipole moment[181] data are in accordance with these structures.

There is some debate concerning the reason for the conformations adopted by the various chlorofluorides. Some authors claim that the stabilization of a particular isomer of $\mathrm{PCl}_{5-n}\mathrm{F}_n$ is a result of $\sigma$ bonding, and is not due to more favourable $\pi$ bonding or *d* orbital participation, though both are present. They suggest that equatorial orbitals, being more electronegative than axial orbitals, give rise to stronger bonds. Electropositive substituents are then associated with the more electronegative phosphorus orbitals (and vice versa), resulting in the observed isomers.[169] However, it is also claimed[170] that the structure of $PF_5$ itself can be explained on the electron pair repulsion theory, without having to make arbitrary assumptions concerning the types of atomic orbitals which take part in the bonding; and similar arguments could presumably be advanced for the chlorofluorides. The true explanation may contain elements of both theories.

In spite of the infra-red evidence, $^{19}F$ nuclear magnetic resonance studies have shown spectroscopic equivalence for all the fluorine atoms in phosphorus(V) fluoride (both gaseous and liquid states)[76–7] as also in a number of mono-substituted compounds $RPF_4$, where R is an alkyl, aryl or trifluoromethane group.[78–9] Conformity of the spectroscopic equivalence of the P–F bonds in phosphorus(V) fluoride with the electron diffraction evidence of a trigonal bipyramidal structure is proposed on the basis of internal pseudo-rotation,[80] or of rapid interchange between the trigonal bipyramid and related tetragonal pyramid configurations.[78–9] For the compounds $R_2PF_3$ and $R_3PF_2$, nuclear magnetic resonance evidence is consistent with a trigonal bipyramidal structure with the substituent groups located in the planar positions. In cyclic $(CH_2)_4PF_4$, rapid intramolecular exchange between apical and planar F-atoms is thought to occur.[78–9]

## Chemical Properties

Phosphorus(V) fluoride behaves as an acceptor for fluoride ion in hydrofluoric acid solution. Evaporation of such solutions with less than the equivalent amount of silver, sodium, potassium, barium or calcium fluoride results in complete conversion to the respective hexafluorophosphate, and absence of solvolysis indicates that phosphorus pentafluoride in this medium is a reasonably strong acid.[81–2] However, in extraction experiments with *m*- and *p*-xylenes in *n*-heptane solution, phosphorus(V) fluoride in hydrogen fluoride ranks as a weak acid, and tantalum or niobium pentafluoride in hydrogen fluoride as a strong acid. The differences were attributed to the comparative ease of attaining the octahedral anion structure, the former only by expansion of the valence shell, but the last pair presumably by use of an available *d*-orbital.[83]

Hexafluorophosphates are formed with nitryl fluoride[84] and with chloryl fluoride[85]: the product of the first reaction, $NO_2PF_6$, is a white solid, that from the second, $ClO_2PF_6$, boils at −35°C. under high vacuum. Similarly chlorine trifluoride forms $ClF_2PF_6$ which is ionic both in the solid state, and in solvents such as chlorine trifluoride. Its heat of dissociation $\Delta H° = 16{\cdot}4$ kcal./mole.[171] In forming 1:1 adducts with ethers, thioethers, selenoethers, aldehydes, ketones, sulphoxides, esters, nitriles and amines,[172–3] phosphorus pentafluoride behaves as a typical Lewis acid. Such products, however, are readily decomposed by water or alcohols and thus are considerably less stable than the corresponding boron trifluoride compounds. Sulpholane for example, which reacts with $BF_3$, is reported to form no stable solid complex with $PF_5$, although the $^{19}F$ magnetic resonance spectrum shows evidence of interaction.[174] The $^{19}F$ magnetic resonance spectra of solutions in acetonitrile are in agreement with an octahedral structure having four equivalent, coplanar fluorine atoms and one apical fluorine atom.[67] The electrical conductance of such solutions is quite high ($\Lambda_c = 210$ ohm$^{-1}$ cm.$^2$ mol.$^{-1}$, $c = 0{\cdot}01$).[175] Like boron trifluoride and tin tetrafluoride, phosphorus pentafluoride is an effective Friedel–Crafts catalyst for the polymerization of *iso*butene or cyanogen chloride.[86] Catalysts consisting of mixtures of phosphorus pentafluoride with up to 50% of metal oxides[87] or with Lewis bases containing oxygen or sulphur[88] are described in the patent literature, as is the use of the fluoride itself in the polymerization of propylene,[89] trioxane[90] and tetrahydrofuran,[67] and in the formation of poly-ethers.[91–2] By rapid cooling of the products of reaction of phosphorus pentafluoride with carbon, substantial yields of tetrafluoroethylene are obtained.[65, 93]

## PHOSPHORUS(V) CHLORO- AND BROMO-FLUORIDES

Phosphorus(V) chloro- and bromo-fluorides occur as unstable covalent liquids or as relatively stable, isomeric, salt-like solids. The first type is obtained by halogen addition to phosphorus(III) halogenofluorides and the second mainly by fluorination of phosphorus(V) halides in a suitable polar solvent; both types of reaction must be carried out in the absence of moisture. A number of such compounds have been described and are summarized in Table V. The properties of the molecular chlorofluorides are summarized in Table VI.

*Table V.—The Phosphorus(V) Chloro- and Bromo-fluorides*

| Covalent halides | | Salt-like halides | |
|---|---|---|---|
| $PCl_5$ | only as vapour, or as liquid under pressure, or as solute in non-polar solvents[74–5] | $[PCl_4]^+[PCl_6]^-$ | colourless crystals, subl. 160°C., m.p. 167°C. under pressure[74–5, 97–8] |
| | | $[PCl_4]^+[PCl_5F]^-$ | colourless crystals, decomp. 110°C.[96] |
| $PCl_4F$ | mobile liquid, m.p. $-63°$, b.p. 67°C.,[94] m.p. $-59$°C.[95] | $[PCl_4]^+F^-$ (or $[PCl_4]^+[PCl_4F_2]^-$ [176]) | colourless crystals, subl. 175°C.[94, 96] |
| $PCl_3F_2$ | m.p. $-63$°C.[95] | — | |
| $PCl_2F_3$ | stable gas, m.p. $-125$°C., b.p. 7·1°C.[7, 41–2, 95–6] | $[PCl_4]^+[PF_6]^-$ | white crystalline powder, subl. 135°C. with decomposition[41, 99] |
| $PClF_4$ | gas, m.p. $-132$°C., b.p. $-43·4$°C., decomp. at room temp.[177] | — | |
| $PBr_5$ | only as solute in non-polar solvents[74–5] | $[PBr_4]^+[Br]^-$ | red-brown crystals, melting with decomposition above 83·8°C.[100–2] |
| $PBr_4F$* | clear liquid, decomp. at room temperature[5, 7] | $[PBr_4]^+[F]^-$ | yellow cryst. powder, m.p. 87°C. with decomposition[7] |
| $PBr_3F_2$* | [5] | — | |
| $PBr_2F_3$ | unstable liquid, decomp. 15°C. (Mellor, VIII, 1042) | $[PBr_4]^+[PF_6]^-$ | white cryst. powder, subl. 135°C. with decomposition[103] |

* Formation indicated, but not further characterized.

Ionic lattice structures are established for crystalline phosphorus pentachloride[97–8] and phosphorus pentabromide,[100–2] each having a tetrahedral cation (approximating $sp^3$ hybridization at the P-atom, with bond lengths P–Cl = 1·98 A., P–Br = 2·2 A.) the former with an octahedral anion ($sp^3d^2$ hybridization, P–Cl = 2·06 A.) and the latter a bromide anion. Typical of the salt-like pentahalides, both compounds behave as electrolytes in polar solvents, and transport experiments in acetonitrile solution have confirmed the presence of $[PCl_4]^+$ and $[PCl_6]^-$ [104] and of $[PBr_4]^+$ and $[PBr_6]^-$ [105] ions respectively.

The covalent chlorofluorophosphoranes are conveniently synthesized in an all-glass apparatus[95] by condensing excess chlorine on the appropriate phosphorus(III) chlorofluoride cooled in liquid nitrogen, and subsequently fractionating *in vacuo* after holding 30 min. at somewhat higher temperatures, $-78°$ for $PCl_4F$ and $PCl_3F_2$, $-127$°C. for $PCl_2F_3$, in order to complete the reaction. Chlorotetrafluorophosphorane, $PClF_4$, cannot be isolated from this reaction, but has been obtained by the controlled fluorination of the molecular form of $PCl_2F_3$, using antimony trifluoride.[177] Fluorotetrachlorophosphorane, $PCl_4F$, can also be conveniently prepared by the action of silver fluoride on phosphorus pentafluoride.[176] The compounds react with excess of pyridine in the liquid phase to form white, thermally unstable, solid complexes; *viz.*, $C_5H_5N,PCl_4F$, $C_5H_5N,PCl_3F_2$ and $3C_5H_5N,PCl_2F_3$, all soluble

*Table VI.—Physical Properties of the Chloro- and Fluoro-phosphoranes*
(data from ref. 105, except where otherwise stated)

| Compound | m.p. (°C.) | b.p. (°C.) | Latent heat of vaporization (kcal./mole) | Trouton const. (e.u.) | Density $d = -A \times 10^{-3}t + B$ ($t$ in °C.) | | Vapour pressure $\log p_{(\mathrm{mm.})} = -\frac{A}{T} + B$ | | Electric dipole moment (gas) | Molar refraction $R_D$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *A* | *B* | *A* | *B* | | |
| $PF_5$ | −91·6 | −84·8 | 4·00 | 21·2 | | | 898·9[66] | 7·646[66] | | 9·2 |
| | (−93·8[66] | −84·6[66] | 4·11[66] | 21·8[66]) | | | | | | |
| $PClF_4$ | −132 | −43·4<br>(extrap.) | 5·16 | 22·5 | | | 1126·893 | 7·78633 | | — |
| $PCl_2F_3$ | −124 | +2·5 | 6·23 | 22·6 | 2·68682 | 1·65702 | 1362·07 | 7·82199 | 0·68[183] | 17·4 |
| | | (+7·1 | 5·66 | 20·7 | | | 1288 | 7·264[41]) | | |
| $PCl_3F_2$ | −61 | 50·4 | 7·56 | 23·4 | 2·20952 | 1·72669 | 1651·28 | 7·98483 | 0·0[183] | 25·4 |
| $PCl_4F$ | −30·5 | 105·9 | 9·00 | 23·8 | 1·88560 | 1·80189 | 1967·71 | 8·07133 | 0·21 | 33·0 |
| ($PCl_5$ | 160 | subl. 159°) | | | | | | | | |

in nitrobenzene.[95] The heats of reaction of phosphorus(V) chloride and chlorofluorides with pyridine to form 1:1 complexes in nitrobenzene solution at 30°C. were: $PCl_3F_2$ 35·3 ± 0·3, $PCl_4F$ 27·0 ± 0·2 and $PCl_5$ 22·0 ± 0·2 kcal. mole$^{-1}$.[106] It was concluded[106–7] that the order of Lewis acid strength towards pyridine was therefore the same as that expected from electronegativity or steric effect considerations, and in fact the reverse of that found earlier[108] (viz. $BBr_3 > BCl_3 > BF_3$) for the boron trihalides. Nuclear magnetic resonance spectra (resolution = 2 c.p.s.) for liquid forms of $PCl_2F$, $PClF_2$, $PCl_4F$, $PCl_3F_2$ and $PCl_2F_3$ at −15°C. and for the 1:1 pyridine adducts of $PCl_4F$ and $PCl_3F_2$ in nitrobenzene solution, consisted of one doublet without any secondary splitting. This evidence supports a common structural model for the phosphorus(V) chlorofluorides, with equivalent fluorine atoms in each compound, and absence of any ionization process involving fluorine for the 1:1 adducts in nitrobenzene.[95] The derived data in Table VII exhibit opposing trends in $^{19}F$ shift with increasing fluorine content in the phosphorus(III) and phosphorus(V) chlorofluorides. Although a trigonal bipyramidal structure has been established[166] for dichlorotrifluorophosphorane in which the 2 chlorine atoms occupy equatorial positions, complete assignment for the tetrachloro- and trichlorofluorophosphoranes is made more difficult by the apparent spectroscopic equivalence of all the fluorine atoms in phosphorus(V) fluoride,[76–9] and by the very small chemical shift (0·07 p.p.m.) for the difference between apical and equatorial fluorine atoms in trifluoromethyltetrafluorophosphorane.[78–9] A similar study of dichloro- and dibromo-trifluorophosphorane, $PCl_2F_3$ and $PBr_2F_3$, shows that there are two fluorine environments at very low temperatures, which become equivalent at ambient temperatures. The intramolecular exchange activation energy of both compounds is about 7·2 kcal./mole.

*Table VII.—$^{19}$F Nuclear Magnetic Resonance Data for the Phosphorus(III), (V) and Phosphoryl Chlorofluorides*

| Compound | Chemical shift from $CF_3COOH$ p.p.m. | P–F coupling constant c.p.s. |
|---|---|---|
| $PF_5$ | −5·0 | 930 |
| $PCl_2F_3$ | −108·0 | 1048 |
| $PCl_3F_2$ | −191·8 | 1045 |
| $PCl_4F$ | −220·0 | 996 |
| $PBr_2F_3$ | −135·0 | 1124 |
| $PF_3$ | −43·4 | 1400 |
| $PClF_2$ | −39·9 | 1390 |
| $PCl_2F$ | −20·7 | 1320 |
| $C_5H_5N,PCl_3F_2$ | −101·8 | 983 |
| $C_5H_5N,PCl_4F$ | −140·0 | 1049 |
| $POF_3$ | 15·8 | 1055 |
| $POClF_2$ | −30·4 | 1120 |
| $POCl_2F$ | −69·0 | 1175 |

Data for $PF_5$, $PF_3$ and $POCl_xF_{3-x}$ are taken from references 78–9.
Data for the two resonances shown by the apical and equatorial fluorine atoms in $PCl_2F_3$ and $PBr_2F_3$ are given in reference 179.
The $^{31}P$ spectrum of $PCl_4F$ consists of a sharp doublet with chemical shift −56 ± 2 p.p.m. relative to 85% $H_3PO_4$ and a coupling constant of 1010 ± 25 c.p.s.

Beginning with the 'covalent' and then passing to the 'salt-like' group, the more important members of the phosphorus(V) halogenofluorides (cf. Table V) will be discussed individually.

### *Dichlorotrifluorophosphorane, $PCl_2F_3$*

The formation reaction from gaseous phosphorus trifluoride and chlorine is photosensitive and catalyzed by glass surfaces. Raising the temperature from 0 to

25°C. reduces the reaction rate by about half, while at low temperatures in the liquid state the reaction is many times more rapid.[42] Preparation is carried out with slight excess of phosphorus trifluoride, and pure dichlorotrifluorophosphorane is obtained on repeated fractionation *in vacuo*. Varying small amounts of mixed white solid tetrachlorophosphonium hexafluorophosphate, $[PCl_4]^+[PF_6]^-$, and tetrachlorophosphonium fluoride, $[PCl_4]^+[F]^-$, in the molar ratio of approximately 9:1 are also formed.[41] When equilibrium proportions of the liquid reagents contained in a pressure vessel lined with Hastelloy C are allowed to equilibrate at room temperature, pressure versus time measurements are in accord with a fast reaction: $PF_3+Cl_2=PCl_2F_3$, followed by two slow reactions:

$$\begin{array}{lcll} 2PCl_2F_3 & = & [PCl_4]^+[PF_6]^- & \\ 5PCl_2F_3 & = & [PCl_4]^+[PCl_6]^- & +3PF_5 \\ \text{(liquid)} & & \text{(solid)} & \text{(gas)} \end{array}$$

After 140 hr. the bulk of the product is solid, while the volatile fraction is essentially phosphorus pentafluoride.[67]

Vapour pressures from 213 to 263°K. are represented by $\log_{10} p_{\text{mm.}} = 7{\cdot}264 - 1288/T$, from which b.p. (extrapolation to 760 mm.) = 7·1°C., latent heat of vaporization = 5·66 kcal. mole$^{-1}$ and Trouton's constant = 20·2. The m.p. lies between −130° and −125°C. and the vapour density at 20°C. is in accord with that expected from $PCl_2F_3$ molecules.[41] More recent data[183] are given in Table VI. Peaks in the infra-red spectra at 40 and 80 mm. pressure are observed at:

$$\left.\begin{array}{llllllll} 932 & \text{s.} & 675 & \text{s.} & 564 & \text{m.} & 492 & \text{m.} \\ 899 & \text{s.} & 668 & \text{s.} & 530 & \text{s.} & 432 & \text{w.} \\ 870 & \text{s.} & 635 & \text{s.} & 500 & \text{m.} & 415 & \text{m.} \end{array}\right\} \text{cm.}^{-1}$$

Mass spectroscopy gives $PF_3Cl_2^+$, $PF_3Cl^+$, $PF_2Cl^+$, $PF_3^+$, $PClF^+$, $PF_2^+$ and $Cl^+$ ion species at an ionization energy of 15 e.v. From these results it appears that loss of fluorine occurs only from monochloro fragments.[41] Nuclear quadrupole resonance[180, 178] and spectroscopic[166] data are in accordance with a structure in which the chlorine atoms lie in the equatorial plane, and not axially as suggested by previous workers.[16] The asymmetric structure is supported by the high value of the gas-phase dipole moment of $PCl_2F_3$ (0·68 D) compared with that of $PCl_4F$ (0·21 D),[182] and the zero value shown by $PCl_3F_2$.[181]

The specific conductance of liquid dichlorotrifluorophosphorane is $<10^{-7}$ mho cm.$^{-1}$ For 0·0452 and 0·09053 M. solutions in acetonitrile at 20°C., molar conductances are 9·63 and 9·31 mho cm.$^2$ mole$^{-1}$, respectively[41] (cf. 90·9 mho cm.$^2$ mole$^{-1}$ for a 0·042 M. solution of the salt-form analogue $[PCl_4]^+[PF_6]^-$ at 30°C.[99]), i.e. of the order for limited ion formation.

Above 150°C. disproportionation of dichlorotrifluorophosphorane occurs, giving tetrachlorofluorophosphorane and phosphorus pentafluoride: $2PCl_2F_3 = PCl_4F + PF_5$ (cf. Mellor, VIII, 1042), but this is complicated by the reactions:

$$\begin{array}{rcl} PCl_4F+PF_5 & = & [PCl_4]^+[PF_6]^- \\ \text{and } PCl_4F & = & [PCl_4]^+[F]^- \end{array}$$

and also by the formation of phosphoryl fluoride and silicon tetrafluoride resulting from attack on the glass apparatus.[96]

*Dibromotrifluorophosphorane*, $PBr_2F_3$. The stability of the halogenofluorophosphoranes is decreased by substitution of bromine for chlorine. Thus dibromotrifluorophosphorane decomposes at 15°C. while the corresponding dichloro-compound is stable up to 200°C.[7]

*Tetrachlorofluorophosphorane*, $PCl_4F$, f.p. −63°, b.p. +67°C. may be obtained by distillation of tetrachlorophosphonium fluoride, $[PCl_4]^+[F]^-$,[109] or of the pyrolysate of tetrachlorophosphonium hexafluorophosphate, $[PCl_4]^+[PF_6]^-$,[94] both in arsenic(III) chloride suspension at 70° to 90°C.

The isomerization $PCl_4F \rightarrow [PCl_4]^+[F]^-$ is a first-order reaction with rate constants 5·62, 3·02, 1·58 and $0{\cdot}843\times10^{-4}$ min.$^{-1}$ at 30, 20, 10 and 0°C., respectively.

The activation energy, attributed to exchange of chlorine between apical and equatorial positions, is 10·6 kcal. mole$^{-1}$ and the frequency factor is 4·37 min.$^{-1}$ [109] A more recent study by infra-red, cryoscopic and conductivity methods suggests that the ionic form of $PCl_4F$ is in fact tetrachlorophosphonium difluorotetrachlorophosphate, $[PCl_4^+][PCl_4F_2^-]$, contaminated by traces of $[PCl_4^+][PF_6^-]$ and $[PCl_4^+][PCl_6^-]$.[176] Values of the equilibrium constant for the dissociation:

$$PCl_4F(g) \rightleftharpoons PCl_2F(g) + Cl_2(g)$$

are:

| °C. | 133·8 | 148·0 | 163·5 | 182·3 | 193·5 | 212·5 |
|---|---|---|---|---|---|---|
| $\log_{10} K_{p(\text{min.})}$ | −0·6120 | −0·6630 | +0·1701 | 0·4060 | 0·7593 | 0·9393 |

from which $\Delta H = 11$ kcal. mole$^{-1}$,[96] cf. 22 kcal. mole$^{-1}$ for:

$$PCl_5(g) = PCl_3(g) + Cl_2(g)^{31}$$

*Tetrabromofluorophosphorane*, $PBr_4F$, is formed as a clear liquid by passing bromine vapour in a nitrogen gas stream through liquid phosphorus(III) dibromofluoride at −75°C. It decomposes at room temperature into phosphorus(V) bromide and fluoride.[7]

*Tetrachlorophosphonium hexafluorophosphate*, $[PCl_4^+][PF_6^-]$, is a white hygroscopic salt subliming at 135°C. with partial decomposition. It is obtained in quantitative yield by the dropwise addition of arsenic(III) fluoride to a stirred solution of phosphorus(V) chloride in arsenic(III) chloride at room temperature:

$$[PCl_4^+][PCl_6^-] + 2AsF_3 = [PCl_4^+][PF_6^-] + 2AsCl_3$$

Its formation is proposed[99] as confirmatory evidence of the nature of the ionization of phosphorus(V) chloride in polar solvents. The specific conductance of acetonitrile solutions at 30°C. increases linearly with concentration over the range 0·02 to 0·05 M. giving molar conductance values of 40·9 and 94·8 mho cm.$^2$ mole$^{-1}$ at 0·0208 and 0·0485 molality, respectively.[99]

Hydrolysis in aqueous alkali leads to hexafluorophosphates:

$$3[PCl_4^+][PF_6^-] + 7KOH = K_2HPO_4 + 4KCl + KPF_6 + 3H_2O$$

Reaction with arsenic(III) fluoride at room temperature is a convenient source of phosphorus pentafluoride:

$$3[PCl_4^+][PF_6^-] + 4AsF_3 = 6PF_5 + 4AsCl_3{}^{99}$$

Similarly a suspension of tetrachlorophosphonium hexafluorophosphate in either arsenic(III) chloride or carbon tetrachloride under reflux evolves phosphorus pentafluoride and dichlorotrifluorophosphorane, while tetrachlorofluorophosphorane, b.p. 67°C., is retained by the reflux condenser. If the residue from the arsenic chloride reaction is filtered while hot, and then allowed to stand overnight at 0°C. it deposits crystals of tetrachlorophosphonium fluoride containing some hexafluorophosphate. The residue from the reaction in carbon tetrachloride, however, comprises a mixture of tetrachlorophosphonium fluoride and tetrachlorophosphonium pentachlorofluorophosphate.[94, 96] Heating tetrachlorophosphonium hexafluorophosphate *in vacuo* at 100° to 150°C. gives dichlorotrifluorophosphorane; at higher temperatures the products are those arising from disproportionation of this compound and side reactions with the glass apparatus.[96]

*Tetrachlorophosphonium fluoride*, $[PCl_4^+][F^-]$ (or $[PCl_4^+][PCl_4F_2^-]$[176]), is a white hygroscopic solid, subl. 175°C., m.p. 177°C. under pressure. It may be obtained from tetrachlorophosphonium hexafluorophosphate by decomposition in arsenic(III) chloride suspension at 70° to 85°C. under reflux as outlined above. The solid separating from the liquid phase at 0°C. is freed from arsenic(III) chloride and tetrachlorophosphonium hexafluorophosphate impurities by heating up to 80°C. under 1 mm. pressure.[94]

Reaction with phosphorus pentafluoride is rapid at 50°C. according to the equation $[PCl_4^+][F^-]+PF_5=[PCl_4^+][PF_6^-]$. Cryoscopy in acetic acid gives mol. wt. = 80 (*cf.* half formula weight = 96). Hydrolysis in aqueous alkali gives one third of the fluorine as monofluorophosphate, i.e. it requires 6·7 equivalents of caustic soda per mole instead of 7 according to the equation:

$$[PCl_4^+][F^-]+7NaOH = Na_2HPO_4+4NaCl+NaF+3H_2O$$

The specific conductance of tetrachlorophosphonium fluoride solutions in acetonitrile at 21°C. increases linearly with concentration over the range 0·05 to 0·1 M. giving molar conductance values of 15·8 and 25·5 mho cm.$^2$ mole$^{-1}$ at 0·0501 and 0·1031 M., respectively. The specific conductances for the melt at 190°C. under pressure and for liquid tetrachlorofluorophosphorane are 0·16 and $2{\cdot}0\times10^{-6}$ mho cm.$^{-1}$, respectively.[94]

Reversion of molten tetrachlorophosphonium fluoride to the crystalline form occurs only slowly at 20°C. under sealed tube conditions and subsequent remelting takes place at an appreciably lower temperature, viz. 161° against the original 177°C. Some tetrachlorophosphonium hexafluorophosphate crystallizes from the melt. The equilibria are expressed[94] by:

$$\text{(i)}\qquad \underset{\text{(solid)}}{[PCl_4]^+[F]^-} \underset{\text{slowly at 0° to 30°C.}}{\overset{\text{at 177°C. (closed tube)}}{\rightleftharpoons}} \underset{\text{(liquid)}}{PCl_4F}$$

$$\text{(ii)}\qquad \begin{cases} 5PCl_4F \rightleftharpoons 4PCl_5+PF_5 \\ PCl_4F+PF_5 \rightleftharpoons [PCl_4]^+[PF_6]^- \end{cases}$$

*Tetrachlorophosphonium pentachlorofluorophosphate*, $[PCl_4]^+[PCl_5F]^-$. The solid product from the decomposition of tetrachlorophosphonium hexafluorophosphate in boiling carbon tetrachloride loses tetrachlorophosphonium fluoride when heated at 85°C. in dry air. The residue had an analysis corresponding to $PCl_{4\cdot5}F_{0\cdot5}$ and a unique *X*-ray powder pattern.[96] Molar conductance values in acetonitrile at 20°C. were 72·2, 68·5 and 66·1 mho cm.$^2$ mole$^{-1}$ for 0·0227, 0·0433 and 0·0685 molar solutions, respectively, and transport experiments confirmed the presence of both phosphorus and fluorine in the anion which had a transport number close to 0·5. Above 110°C. disproportionation to phosphorus pentachloride and tetrachlorofluorophosphorane occurred.[96]

Mass spectroscopy at an ionization energy of 50 e.v. gave ion species derived from a $P_2X_{10}$ parent thus:

| | | | | |
|---|---|---|---|---|
| $P_2Cl_8F^+$ | $P_2Cl_7F^+$ | $P_2Cl_6F^+$ | $P_2Cl_5F^+$ | $P_2Cl_3F^+$ |
| $P_2Cl_2F^+$ | $P_2ClF^+$ | $P_2Cl_2^+$ | $PCl_4^+$ | $PCl_3^+$ |
| $PCl_2^+$ | $PClF^+$ | $PCl^+$ | $Cl^+$ | $P^+$ |

The equilibrium

$$\underset{\text{(solid)}}{[PX_4]^+[PX_6]^-} \rightleftharpoons \underset{\text{(vapour)}}{P_2X_{10}}$$

is suggested to account for this cracking pattern.[110] The $P_2X_{10}$ and derived $P_2$ ion species contain Cl-bridges in a 4-membered ring with octahedrally connected phosphorus atoms (*cf.* phosphorus pentachloride, page 478).

*Tetrabromohexafluorophosphonate*, $[PBr_4]^+[PF_6]^-$, is formed as a white hygroscopic crystalline solid (subl. 135°C. with decomposition) by the dropwise addition of arsenic(III) fluoride to a stirred suspension of phosphorus(V) bromide in carbon tetrachloride or carbon disulphide at 30° to 50°C. In contact with arsenic(III) fluoride the formation of $[PBr_4]^+$ and $[PBr_6]^-$ ions is postulated[103] and fluorination of the cation follows. With phosphorus(V) bromide in arsenic(III) chloride solution, halogen exchange occurs and white tetrachlorophosphonium hexafluorophosphate is the main product of subsequent fluorination with arsenic(III) fluoride.[103]

Tetrabromophosphonium hexafluorophosphate is readily soluble in both phosphorus and arsenic(III) chlorides or bromides. The chloride solutions slowly deposit tetrachlorophosphonium hexafluorophosphate on standing, while the bromide solutions decompose on warming to give phosphorus(V) fluoride thus:

$$[PBr_4][PF_6] \xrightarrow[\text{in AsCl}_3\text{ at 20°C.}]{} [PCl_4][PF_6]$$

$$[PBr_4][PF_6] \xrightarrow[\text{in AsBr}_3\text{ at > 30·8°C.}]{} [PBr_4][F] + PF_5$$

$$\hookrightarrow \tfrac{4}{5}PBr_5 + \tfrac{1}{5}PF_5$$

$$cf.\quad [PCl_4][PF_6] \xrightarrow[\text{in AsCl}_3\text{ at > 70°C.}]{} PCl_4F + PF_5$$

The specific conductance of tetrabromophosphonium hexafluorophosphate solutions in arsenic(III) fluoride at 0°C. increases linearly with concentration over the range 0·0186 to 0·0832 M; molar conductances at these concentrations are 46·2 and 42·4 mho cm.$^2$ mole$^{-1}$ respectively. In water alone, hydrolysis is vigorous and leads to free bromine and reduced acids. With sodium acetate buffer or with excess of alkali, no bromine is liberated and $PF_6^-$, $PO_2F_2^-$, $PO_3F^{2-}$ and $PO_4^{3-}$ anions are formed.[103]

*Tetrabromophosphonium fluoride*, $[PBr_4]^+[F]^-$, m.p. 87°C. (decomp.), separates as a yellow powder from tetrabromofluorophosphorane after about 16 hr. at $-75°$ to $-30°$C. By conducting the process in carbon tetrachloride solution, bright yellow crystals of composition $[PBr_4][F],2CCl_4$ are obtained, which lose two carbon tetrachloride molecules when under vacuum at room temperature. Both compounds give conducting solutions in acetonitrile and cryoscopic measurements correspond to half and quarter formula weights, respectively. Hydrolysis is vigorous and free bromine forms in acid solution. With excess of alkali no bromine is formed and the hydrolysate contains $PO_4^{3-}$, $PO_3F^{2-}$, $F^-$ and $Br^-$ anions.[7]

## PHOSPHORYL FLUORIDE, PHOSPHORYL CHLORO- AND BROMO-FLUORIDES

### Preparation

Phosphoryl halogenofluorides are obtained from phosphoryl chloride or bromide ($POX_3$) by methods analogous to those for obtaining phosphorus(III) halogenofluorides from phosphorus(III) chloride or bromide ($PX_3$). Thus fluorination of $POX_3$ can be effected, (*a*) at reduced pressure in the vapour state, with heated calcium fluoride pellets; or (*b*) at temperatures between 75°C. and the boiling point by controlled addition of powdered antimony(III) fluoride in the presence of antimony(V) fluoride catalyst[111]; or (*c*) by refluxing with ammonium fluoride;[2] or (*d*) by passing through mixed alkali metal fluoride melts.[135] Relative yields where X = chlorine are indicated by the methods (*a*), (*b*) and (*c*), respectively, in Table VIII.

*Table VIII.—Fluorination of Phosphoryl Chloride or Bromide* ($POX_3$)

| X | Method (see text) | Atom ratio P:F:X in original mixture | Temp. °C. | Yield, wt. % of volatile product | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $PF_3$ | $POF_3$ | $POF_2X$ | $POFX_2$ | $POX_3$ | |
| Cl | a | — | 200 | — | 90 | ←··········10··········→ | | — | 111 |
| | | | 150 | — | 35 | 25 | 40 | — | |
| Cl | b | — | 75 | — | 55 | 5 | 40 | — | 111 |
| Cl | c | — | ~107 | — | 63 | 11 | 26 | — | 2 |
| Cl | d | 4:3:Nil | 600 | 4 | 84 | — | — | — | 1 |
| | | 4:3:3 | 600 | 26 | 51 | — | — | — | |
| | | 4:1·5:1·5 | 500 | 3·7 | 26·8 | 22·4 | 21·0 | 13·5 | |
| Br | e | — | 60–100 | — | 60 | 10 | 30 | — | 112 |

Phosphorus pentoxide–calcium fluoride mixtures at 500° to 600°C. give phosphoryl fluoride, but in the presence of sodium chloride, and in iron reaction vessels, phosphoryl fluorochlorides and phosphorus(III) fluoride are also formed ('d' Table VIII). Trace amounts of water give rise to hydrogen fluoride or chloride among the volatile products; with calcium fluoride alone, the amount of phosphoryl fluoride formed closely corresponds to the equation $3CaF_2+4P_2O_5=2POF_3+3Ca(PO_3)_2$.[1, 113] Other effective fluorinating agents for phosphoryl chloride are potassium fluoride in liquid sulphur dioxide[3] and anhydrous hydrofluoric acid.[114] Phosphorus pentoxide dissolves in a large excess of hot iodine pentafluoride[115] or reacts on dropwise addition of fluorosulphonic acid,[116] both with formation of phosphoryl fluoride. The reactions are thought to be:

$$P_2O_5+3IF_5 = 2POF_3+3IOF_3$$

and

$$P_2O_5+3HSO_3F = POF_3+HPO_3+2SO_3+H_2SO_4$$

The latter proceeds to 80% in the presence of excess of phosphorus pentoxide. Phosphoryl fluoride and phosphoryl fluorobromides are obtained[112] from the usual fractionation methods following slow addition of powdered antimonous fluoride to phosphoryl bromide at 25 to 50 mm. pressure. The initial reaction is vigorous at 60°C., proceeding without added catalyst on gradually raising the temperature to 100°C. Relative yields are indicated at 'e' Table VIII.

### Physical Properties

Physical data for the phosphoryl fluorides are summarized in Table IX.

Electron diffraction measurements[16, 117–8] point to tetrahedral structures for the phosphoryl halides, approximating $sp^3$ hybridization at the P-atom. The molecular data are summarized in Table X together with those derived from measurements of pure rotational transitions in the microwave region.[119–21] Observed P–F, P–Br and P–O distances are appreciably shorter than the calculated values for the respective single and double bonds, and hypothetical resonance structures for $POF_3$ have been suggested. Multiple bonding amounting to 0·8 to 2 $\pi$ bonds per P-atom is calculated for the phosphoryl halides from bond length, and from thermochemical data.[122–3] The observed P–Cl distances, however, allow for little or no $\pi$ bond shortening, and in the case of phosphoryl chloride all the multiple bonding character of the P-atom would appear to be contained in the P–O bond. For P–F and P–Br bonds, such shortening corresponds to approximately $\frac{1}{3}\pi$ bond per $\sigma$-bond.[122–3] Bond order calculations[124] based on force constants derived from their vibration spectra, gave values of 2·34, 2·09 and 2·02 for phosphoryl fluoride, chloride and bromide respectively; these are taken to imply a tendency to achieve a closed shell structure of 12 rather than 8 electrons in these compounds. Fundamental frequency assignments for a number of the phosphoryl and thiophosphoryl halides were made[27–8, 125, 184, 186] on the basis of their infra-red and Raman spectra. Force constant data evaluated by Wilson's method of matrices are summarized in Table XI and some authors[125–6] have attempted more complete solutions by using available data for the corresponding $PX_3$ halide.

The same authors give heat content, free energy, entropy and heat capacity values for both $POX_3$ and $PSX_3$ molecules (ideal gas state, 1 atm. pressure) at temperatures between 50° and 1000°K., calculated by a rigid rotator, harmonic oscillator approximation from their probable absorption frequencies. For the reaction:

$$PX_3(g)+\tfrac{1}{2}O_2(g) = POX_3(g)$$

comparison of the derived $\Delta H$, viz. $-63{\cdot}3$ kcal. mole$^{-1}$ for X=Cl (*cf.* $-68{\cdot}3$ kcal. using the more recent data[31]) with the experimentally determined value $-70{\cdot}6$ kcal. mole$^{-1}$ for X=F was taken[129] as indicating a strengthening of the P–O bond by substitution of fluorine for chlorine. A nuclear magnetic resonance study of the series $POF_3$, $POF_2Cl$, $POFCl_2$, $POCl_3$, showed that with increasing substitution of the more electronegative atom (fluorine) by the less electronegative, the $^{31}P$ resonance

Table IX.—Physical Properties of the Phosphoryl Fluorides

| Compound | $POF_3$ | | $POF_2Cl$ | $POFCl_2$ | $POF_2Br$ | $POFBr_2$ |
|---|---|---|---|---|---|---|
| Reference | 111 | 1 | 111 | 111 | 112 | 112 |
| b.p. °C. | −39·8 | −39·7 | 3·1 | 52·9 | 30·5 | 110·1 |
| m.p. °C. | −39·4 | −39·1 (785 mm.) | −96·4 | −80·1 | −84·8 | −117·2 |
| subl. p. °C. | — | −39·5 (765 mm.) | — | — | — | — |
| Liquid density at 0°C. | — | — | 1·6555 | 1·5931 | 2·099 | 2·568 |
| Critical temperature °C. | 73·3 | — | 150·6 | — | — | — |
| Critical pressure atm. | 41·8 | — | 43·4 | — | — | — |
| Heat of sublimation, kcal. | — | 9·15 | — | — | — | — |
| Heat of vaporization, kcal. | 5·03 | 5·55 | 6·09 | 7·40 | 7·09 | 7·52 |
| Heat of fusion, kcal. | — | 3·60 | — | — | — | — |
| Trouton's constant | 21·6 | 23·8 | 22·0 | 22·7 | 23·4 | 19·6 |
| Vapour pressure constants, where $\log_{10} p_{\text{mm.}} = B - A/T$ | | Solid Liquid | | | | |
| $A$ | 1097·88 | 1984·7 1207 | 1328·3 | 1618·2 | 1550·0 | 1642·9 |
| $B$ | 7·5900 | 11·3755 8·0524 | 7·6904 | 7·8440 | 7·9662 | 7·1687 |
| Temperature range ($T$ = °K.) | 229·3–237·9 | 188–233 233–253 | 211·0–288·2 | 243·1–332·4 | 220·0–306·3 | 300·1–384·6 |

signal is shifted to a lower field, while in the series $POCl_3 \rightarrow POBr_3$ the reverse is true. This was explained by the decreasing effect of the more electronegative ligands in screening the phosphorus nucleus, and also by a double bonding character of the P–F bond.[185]

*Table X.—Molecular Data for the Phosphoryl Halides*

| Compound | Reference | Bond length A. | | | | Bond angle XPX | Dipole moment |
|---|---|---|---|---|---|---|---|
| | | P–O | P–F | P–Cl | P–Br | | |
| $POF_3$ | 16 | 1·56 ± 0·03 | 1·52 ± 0·02 | — | — | 107 ± 2° | — |
| | 119–21 | 1·45 ± 0·03 | 1·52 ± 0·02 | — | — | 102·5 ± 2° | 1·74 ± 0·04 |
| $POF_2Cl$ | 16 | 1·55 ± 0·03 | 1·51 ± 0·03 | 2·01 ± 0·04 | — | 106 ± 3° | — |
| $POFCl_2$ | 16 | 1·54 ± 0·03 | 1·50 ± 0·03 | 1·99 ± 0·04 | — | 106 ± 3° | — |
| $POCl_3$ | 117 | 1·45 ± 0·05 | — | 1·99 ± 0·02 | — | 103·5 ± 1° | — |
| | 119–21 | 1·45 ± 0·03 | — | 1·99 ± 0·02 | — | 103·6 ± 2° | — |
| $POBr_3$ | 118 | 1·41 ± 0·07 | — | — | 2·06 ± 0·03 | 108 ± 3° | — |

*Table XI.—Force Constants* ($10^5$ *dynes/cm.*) *for the Phosphoryl Halides*

| Compound | Reference | $f_D$ | $f_d$ | $f_{dd}$ | $f_\alpha - f_{\alpha\alpha}$ | $f_\beta - f_{\beta\beta}$ | $f_{\alpha\alpha} + f_{\beta\beta}$ |
|---|---|---|---|---|---|---|---|
| $POF_3$ | 27 | 11·4 | 6·18 | 0·79 | 0·841 | 0·365 | 0·052 |
| | 28 | 10·95 | 6·31 | 0·47 | 0·475 | 0·639 | — |
| $POCl_3$ | 127 | 9·6 | 2·87 | 0·575 | 0·317 | 0·23 | 0·0034 |
| | 28 | 10·38 | 2·56 | 0·257 | 0·263 | 0·295 | — |
| | | $f_D$ | $f_d$ | $f_{dd}$ | $f_{Dd}$ | $f_\alpha$ | $f_\beta$ |
| $POCl_3$ | 128 | 9·554 | 2·345 | 0·695 | 0·550 | 0·240 | 0·435 |
| $POBr_3$ | 128 | 9·974 | 1·892 | 0·437 | 0·513 | 0·216 | 0·254 |
| $PSCl_3$ | 128 | 5·363 | 2·078 | 0·437 | 1·456 | 0·247 | 0·728 |

## Chemical Properties

The phosphoryl halogenofluorides are colourless in all states when pure; they are hydrolyzed by moist air and react vigorously with water. Dry phosphoryl fluoride gas undergoes only slight decomposition in contact with glass, copper or carbon at 600°C. or silicates at 900°C. With iron at 600°C., slow reduction to phosphorus(III) fluoride occurs; with steel wool at 950°C. absorption is complete, solid products being formed.[1] With carbon at 950°C., decomposition occurs to phosphorus(III) fluoride, carbon monoxide, small amounts of phosphorus and an unidentified gas thought to be carbon tetrafluoride.[1] Difluorodiazine converts phosphoryl fluoride to phosphorus(V) fluoride[156]

$$POF_3 + N_2F_2 \rightarrow PF_5 + N_2 + O_2$$

whilst $\cdot NF_2$ radicals from the photolytic decomposition of $N_2F_4$ yield nitrosonium hexafluorophosphate, $[NO^+][PF_6^-]$.[187]

Phosphoryl fluoride hydrolyzes in a stepwise manner according to the scheme:

$$POF_3 \xrightarrow[+H_2O]{} HOPOF_2 \xrightarrow[+H_2O]{} (HO)_2POF \xrightarrow[+H_2O]{} (HO)_3PO + 3HF$$

It is possible, after conducting the reaction in weakly basic solution, to isolate the intermediate acids as their nitron salts.[130]

Evidence of the probable formation of a 1:1 addition compound $F_3PO,BF_3$, f.p. about −20°C., comes from thermal analysis of the phosphoryl fluoride–boron trifluoride system.[50] Phosphoryl chloride and phosphoryl dichlorofluoride form 2:1 addition compounds with zirconium and hafnium tetrachlorides which decompose at

50° to 60°C. *in vacuo* to the 1:1 compound and phosphoryl halide. Phosphoryl monochlorofluoride and phosphoryl fluoride, however, form 1:1 compounds only. The respective m.p., etc. in °C. are:

|  | $2POX_3,MCl_4$ |  | $POX_3,MCl_4$ |  |
|---|---|---|---|---|
| M= | Zr | Hf | Zr | Hf |
| $POCl_3$ | decomp. 50–60° | decomp. 50–60° | sublimes 130° | decomp. 145° |
| $POFCl_2$ | 74–78° | 80–83° | 161–163° | 165–167° |
| $POF_2Cl$ | — | — | 116–119° | 110–113° |
| $POF_3$ | — | — | 85° | 85° |

With a more prolonged contact time and in the presence of excess of phosphoryl mono- or dichlorofluorides, halogen exchange occurs and compounds of the type $2POCl_3,MCl_4$ finally separate out.[131]

## HYDROGEN FLUOROPHOSPHORANES

The reaction of anhydrous hydrogen fluoride and hypophosphorous acid at $-22$°C. yields dihydrogentrifluorophosphorane, $PH_2F_3$.[188–90] $PH_2F_3$ is a colourless gas, m.p. $-51$°C.,[188] b.p. (extrap.) $+2$°C.,[188] 3·8°C.[190] The vapour pressure from $-52$ to 0°C. obeys the relation $\log p_{(\text{mm.})} = (-1473{\cdot}0/T) + 8{\cdot}1991$, the heat of vaporization is 6·7 kcal./mole and the Trouton constant 24 e.u.[190] The infra-red spectrum shows absorptions at 328, 389, 471, 655, 765, 820, 867, 995, 1026, 1292, 2465 and 2538 cm.$^{-1}$ In the gaseous state the molecule appears to be a trigonal bipyramid of $C_{2v}$ symmetry with two of the fluorine atoms axial. In the solid and liquid states association through fluorine bridges occurs.[189]

Hydrogen tetrafluorophosphorane, $PHF_4$, is formed analogously from phosphorous acid and anhydrous hydrogen fluoride at $-50$°C., as a colourless gas, m.p. $-89$°C.,[188] b.p. (extrap.) $-37$°C.,[188] $-39{\cdot}0$°C.[190] The vapour pressure is given by $\log p_{(\text{mm.})} = (-1158{\cdot}9/T) + 7{\cdot}8290$, from $-80$° to $-45$°C. the heat of vaporization is 5·30 kcal./mole and the Trouton constant 22·6 e.u.

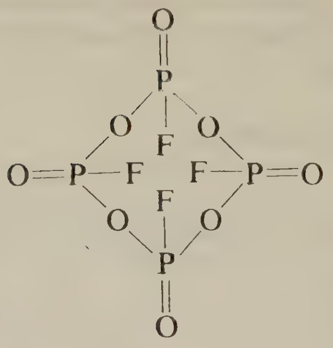
The $^1H$, $^{19}F$ and $^{31}P$ nuclear magnetic resonance spectra suggest that both molecules are undergoing ligand exchange, with retention of P–H and P–F bonding only at the lowest temperatures studied. Both substances react rapidly with quartz or borosilicate glass, and must be studied in metal vacuum systems.[190]

## CONDENSED PHOSPHORYL FLUORIDES

Pyrophosphoryl fluoride, $P_2O_3F_4$, a colourless mobile liquid, m.p. $-0{\cdot}1$°, b.p. 72°C. (extrap.) and phosphorus dioxyfluoride, $(PO_2F)_n$, a white hygroscopic solid, were separated[62] by vacuum fractionation up to 20°C. from the white solid obtained (in as much as 30% yield) by subjecting equimolar mixtures of phosphorus(III) fluoride and oxygen at $-75$° to $-60$°C. to a silent electric discharge. Pyrophosphoryl fluoride boils with decomposition at atmospheric pressure; its vapour pressure between 273° and 318°K. is expressed by $\log_{10} p_{\text{mm.}} = 8{\cdot}957 - 2096{\cdot}7/T$; its molar heat of vaporization is 9581 g.-cal.; Trouton's constant = 27·8 and $d_{20} = 1{\cdot}65$. It undergoes vigorous hydrolysis with water giving difluorophosphoric acid according to the equation $P_2O_3F_4 + H_2O \rightarrow 2F_2PO(OH)$. On heating to 500°C., phosphorus dioxyfluoride decomposes without melting:

$$4(PO_2F) = P_2O_5 + P_2O_3F_4$$

Hydrolysis with water leads to monofluorophosphoric acid $FPO(OH)_2$. It has a crystalline type of *X*-ray powder diagram and is thought[62] to be the cyclic tetramer:



The reaction of phosphoryl dichloride fluoride with phosphorus pentoxide yields small quantities of pyrophosphoryl dichloride difluoride, a colourless liquid, b.p. 36°C./12 mm., $n_D^{20}$ 1·3860, $d_{20}^{20}$ 1·7918.[191] It rearranges if heated at 50°C. for several days, giving phosphoryl dichloride fluoride and a higher polymeric chlorofluoride containing F(Cl)PO–O end groups and $\text{–O–}\underset{\underset{\displaystyle \text{F}}{|}}{\text{P}}\text{(O)–O}$ middle groups.[192] Diethylamine replaces the chlorine atoms only, giving a diethylamide of the formula $O(PO(NEt_2)F)_2$, but ethanol breaks the pyrophosphoryl linkage, giving EtOP(O)ClF.[191]

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## SECTION XIV

# CHLORIDES AND MIXED CHLORIDE HALIDES OF PHOSPHORUS

BY R. H. TOMLINSON

## PHOSPHORUS DICHLORIDE (DIPHOSPHORUS TETRACHLORIDE), $P_2Cl_4$

This substance had been previously described as a colourless, oily, strongly fuming liquid, f.p. $-28$°C. but (in contrast to Mellor, VIII, 998) was not identified[1–2] as a product of subjecting phosphorus(III) chloride–hydrogen mixtures to an electric discharge. Similarly, although metastable species of long life are formed by a micro-wave discharge in phosphorus(III) chloride vapour, they finally react or disproportionate yielding $PCl_5$, $PCl_3$ and subchlorides such as '$P_5Cl$' rather than $P_2Cl_4$.[492] However, when $PCl_3$ was irradiated in a reactor the percentage of $^{32}P$ present as $^{32}PCl_3$ increased with irradiation time, and this effect has been attributed[2] to radiation-induced oxidation of $^{32}P_2Cl_4$ to $^{32}PCl_3$. When phosphorus(III) chloride at $-63$°C. was vaporized through a mercury discharge, red and yellow solids were deposited and small quantities of a volatile liquid product, f.p. $-34$° to $-35$°C., were obtained.[3] The liquid, which decomposed to phosphorus(III) chloride and a yellow non-volatile solid at room temperature, had a composition and molecular weight in agreement with $P_2Cl_4$. Fluorination to give phosphorus difluoride was unsuccessful,[3] as also were similar attempts with phosphorus di-iodide, $P_2I_4$, and various fluorinating agents.[4] In a micro-wave discharge, phosphorus(III) chloride vapour at flow rates of 0·08 g. $PCl_3$/min. at 1 mm. pressure and 1·00 g. $PCl_3$/min. at 5 mm. pressure, was decomposed to extents of 71·5 and 3·5%, respectively.[5] Fractional condensation showed the presence of phosphorus(V) chloride and of red and yellow-tan products with P:Cl atom ratios of 5·5–50:1 and 2·5–5:1, respectively, while retention for 15 hr. at room temperature of all the decomposition products in an evacuated receiver resulted in their complete reversion to phosphorus(III) chloride. Streams of phosphorus(III) chloride vapour mixed with hydrogen in volume ratios $<1:1$ deposited red phosphorus beyond the discharge. A plug of bronze wool placed just beyond the discharge reacted to form cuprous chloride; no phosphorus(V) chloride or red or yellow solids were then deposited in the subsequent cold traps, but phosphorus dichloride was formed in 0·5% yield.[5] In a static system where a 60-cycle discharge was established between bronze wool plugs situated above a pool of phosphorus(III) chloride at 0°C., 75 mg. of phosphorus dichloride were obtained in 15 min., but further conversion was said to be inhibited by poisoning of the bronze.[5] The highest yields of phosphorus dichloride so far reported (viz., 3·5 g./hr) were obtained[6] by subjecting a phosphorus(III) chloride–hydrogen gas stream (optimum mole ratio$=2:1$) at $-78$°C. to a continuous electric discharge between molybdenum electrodes at 7500 v. and pumping out the unreacted hydrogen together with product hydrogen chloride at 19 mm. pressure. Phosphorus dichloride was then separated from the unreacted trichloride by fractional distillation. The authors observed a freezing point closer to $-28$°C. than to $-34$°C.; the density was 1·701 at 0° and the vapour pressure $\sim 1$ mm. at 25°C. The nuclear magnetic resonance spectrum showed a single peak with chemical shift $-155$ p.p.m. relative to 85%

orthophosphoric acid. Mass spectrometry at an ionization potential of 70 e.v. gave[7] the principal ion species as $P_2Cl_4^+$, $P_2Cl_3^+$, $P_2Cl_2^+$, $PCl_2^+$, $P_2Cl^+$, $PCl^+$ and $P_2^+$ with relative abundances of 4·6, 5·3, 1·5, 100·0, 5·8, 36·5 and 9·9, respectively. Probable mechanisms with values of heat of formation for the various ions were deduced; the P–P sigma bond energy was 58 kcal. $mole^{-1}$ which, by comparison with the published value for P–P in $P_4$, was taken[7] as indicative of $\pi$ bonding of the order 1·1 to 1·2$\pi$ bonds/sigma bond.

The infra-red spectrum from 33–1000 $cm.^{-1}$, and the Raman spectrum of phosphorus dichloride have been reported. They are consistent with a *trans*-$Cl_2P$–$PCl_2$ structure, with $C_{2h}$ symmetry, in the solid, liquid and gaseous states.[493]

The hydrolysis of phosphorus dichloride (and di-iodide) has been studied in acid and basic solution under anaerobic conditions. Ionic products were determined by ion exchange chromatography and the results are summarized below.

*Percentage of phosphorus species arising during hydrolysis of dihalides*

| Dihalide | $P_2Cl_4$ | $P_2I_4$ | $P_2Cl_4$ | $P_2I_4$ |
|---|---|---|---|---|
| Conditions | basic | basic | acidic | acidic |
| P Species | | | | |
| $P^1$ anions | 23·7 | 17·2 | 19·5 | 7·5 |
| $P^3$ anions | 14·3 | 14·8 | 52·1 | 73·7 |
| $P^5$ anions | 6·5 | 7·7 | 13·2 | 14·9 |
| Anions containing > 1 P atom | 1·4 | 2·2 | — | — |
| $P_2H_4$ | 50·4 | 53·2 | — | — |
| $PH_3$ | 3·7 | 4·9 | 10·3 | 3·1 |
| P Subhydride | — | — | 4·9 | 0·8 |

These results are compatible with a primary hydrolysis:

$$2P_2X_4 + 2H_2O \rightarrow P_2H_4 + [P_2(OH)_4]$$

followed by further hydrolysis of the unstable hypodiphosphorous acid:

$$[P_2(OH)_4] + H_2O \rightarrow H_3PO_2 + H_3PO_3$$

and dismutation of some of the phosphorous acid:

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

The different results observed in acid solution may be due to oxidation of $P_2H_4$ by hypohalous acid.[494]

Phosphorus dichloride reacts readily with nickel tetracarbonyl.[492, 495] If an excess of the dichloride is used, it behaves as a monofunctional base:

$$Ni(CO)_4 + P_2Cl_4 \rightarrow Ni(CO)_2(P_2Cl_4)_2 \ (+ Ni(CO)(P_2Cl_4)_3\,?)$$

while with excess carbonyl it behaves as a difunctional base:

$$Ni(CO)_4 + P_2Cl_4 \rightarrow (CO)_3Ni - P_2Cl_4 - Ni(CO)_3$$

Equivalent amounts of the two reagents yield polymers containing mono- and difunctional $P_2Cl_4$. $P_2Cl_4$ is more strongly basic towards nickel carbonyl than is $PCl_3$. Iron pentacarbonyl, or chromium or molybdenum hexacarbonyl does not react with phosphorus dichloride.[492]

Phosphorus dichloride undergoes dismutation in the presence of boron tribromide, giving a mixture of phosphorus trihalides and subhalides. Halogen exchange also occurs as far as possible, so that the final product with excess boron tribromide is the complex $PBr_3,BBr_3$.[495] Diborane reacts with phosphorus dichloride yielding hydrogen, boron trichloride, dichloroborane, and subhydrides or subhalides of phosphorus. It may be noted that all the reactions of phosphorus dichloride noted above, with the exception of that with nickel carbonyl, lead to P–P bond fission.[492]

## PHOSPHORUS(III) CHLORIDE

### Preparation

Phosphorus trichloride has been variously obtained by the reduction of phosphoryl chloride vapour with carbon monoxide and active carbon above 400°C.,[8] by the action of chlorine upon calcined phosphate rock, calcium phosphate or phosphoric acid mixtures with carbon and silica[9–18] or of chlorine upon heated ferrophosphorus.[19–23] In the last reaction the volatile complex $FeCl_2,PCl_3$ first formed is decomposed by addition of further ferrophosphorus below red heat. The phosphorus trichloride of commerce is obtained by continuous chlorination of yellow phosphorus in a phosphorus trichloride medium.[24–9] The heat of reaction is dissipated by the reflux rate, and the distillate, which may contain up to 1% of yellow phosphorus, is finally treated in a stirred vessel with just sufficient chlorine to complete the reaction. An apparatus for the laboratory preparation of the pure compound has been described.[30] Phosphorus purified by nitric acid treatment and vacuum distillation has been used as a starting material for this preparation.[496]

### Physical Properties

Molar volumes at 0°K. extrapolated from density measurements at −79°C. for various phosphorus halides and oxyhalides are given[31] as:

| | | |
|---|---|---|
| $PCl_3$ = 67 ml. | $PCl_5$ = 91·5 ml. | $POCl_3$ = 72·1 ml. |
| $PBr_3$ = 76·1 ml. | — | $POBr_3$ = 82·8 ml. |
| $PI_3$ = 93·2 ml. | $PI_5$ = 115 ml. | — |

Vapour pressure and related data for phosphorus trichloride include:

| Range, °C. | $\log_{10} p_{mm.}$ | Latent heat of vaporization kcal. mole$^{-1}$ | b.p. °C. | f.p. °C. | Trouton constant | Ref. |
|---|---|---|---|---|---|---|
| −20 to +70 | $7{\cdot}6455–1657{\cdot}3/T$ | 7·585 (7·415 at 74·7°C.) | 74·7 | −93·6 | 21·3 | 32 |
| 15 to 75 | $7{\cdot}6285–1653{\cdot}6/T$ | 7·57 | 75·2 | | | 33 |
| 19 to 85 | $7{\cdot}472–1600/T$ | 7·32 | 75·3 | | | 34 |

Vapour/liquid equilibrium measurements for the binary system $PCl_3–POCl_3$[35] approximate to ideality; those for the system $PCl_3–SiCl_4$[34] show large deviations from the ideal. The heat capacity of phosphorus trichloride vapour between 298·1 and 1000°K. is given[36] by $C_p^\circ = 20{\cdot}068–0{\cdot}000289T–270600T^2$; the specific heat of the liquid is 28·9 g.-cal. mole$^{-1}$ at 25°C.[33]

Remeasurement of the heat of hydrolysis for the reaction:

$$PCl_3(l) \rightarrow H_3PO_3(aq.) + 3HCl(aq.)$$

together with available thermal data, gave values of $\Delta H$ and $\Delta H^\circ_{f25}$ in kcal. mole$^{-1}$ as −67·5 ± 0·03 and −79·6[37] and as −67·7 and −79·4,[38] respectively. The preferred value for the heat of formation of phosphorus trichloride liquid, viz.: $\Delta H^\circ_{f25} = -74{\cdot}4$ kcal. mole$^{-1}$,[39] has been derived from the hydrolysis–oxidation reaction:

$$PCl_3(l) + Br_2(aq.) \rightarrow H_3PO_4(aq.) + 3HCl(aq.) + 2HBr(aq.)$$

so avoiding the use of uncertain data for $H_3PO_3$(aq). (The value of −81 kcal. mole$^{-1}$ listed[40–2] is based on the original heat of hydrolysis measurements (Mellor, VIII, 1001).) The standard heat ($\Delta H^\circ_f$), free energy ($\Delta G^\circ_f$) and equilibrium constant of formation (log $K_f$) for phosphorus trichloride vapour at 25°C. are given[40–2] as −73·22, −68·42 (both in kcal. mole$^{-1}$) and 50·151, respectively. Enthalpy and free energy functions at 100° intervals from 298·1–1000°K. derived[43–4] from equilibrium and spectroscopic data are reproduced in Table I.

*Table I.—Thermodynamic Functions of* $PCl_{3(g)}$ *in Ideal Gas State*[41]

| $T$°K. | $-\frac{G^\circ - H^\circ_0}{T}$ g.-cal. mole$^{-1}$ deg.$^{-1}$ | $H^\circ - H^\circ_0$ g.-cal. mole$^{-1}$ | $S^\circ$ g.-cal. mole$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|
| 298·1 | 61·66 | 3·840 | 74·54 |
| 350 | 63·75 | 4·740 | 77·29 |
| 400 | 65·61 | 5·650 | 79·74 |
| 500 | 68·87 | 7·500 | 83·87 |
| 600 | 71·68 | 9·400 | 87·35 |
| 700 | 74·09 | 11·320 | 90·26 |
| 800 | 76·30 | 13·260 | 92·88 |
| 900 | 78·31 | 15·210 | 95·21 |
| 1000 | 80·67 | 17·160 | 97·23 |

Equations for the calculation of standard free energies of formation at temperatures up to 1800°C. have been proposed.[45]

Ebullioscopy indicates compound formation with dissolved tin(IV), arsenic(III) and titanium(IV) chlorides; with anthracene as solute the ebullioscopic constant $K = 50$.[46]

The dielectric constant of phosphorus(III) chloride decreases from 3·498 at 17°C. to 3·139 at 59·8°C.[47] Dielectric constant measurements for dilute solutions in carbon tetrachloride, benzene and dioxan have led to dipole moment values (Debye units) for phosphorus(III) chloride and bromide as follows:

| | $PCl_3$ | $PBr_3$ | Ref. |
|---|---|---|---|
| carbon tetrachloride | 0·80, 1·00 | 0·61, 0·52 | 48, 49 |
| benzene | 0·90, 1·16* | — | 50 |
| dioxan | 1·89 (0·01014 M) | 1·65 (0·01142 M) | 51 |
| | 1·49 (0·03819 M) | 1·33 (0·03572 M) | |

* From polarization at 25°C. and refractivity.

The high values in dioxan solution are thought to arise from co-ordination with the solvent.[51] Calculations based on the molecular orbital theory and observed values of dipole moment[52] have given the percentage hybridization of the *p*-orbitals of the phosphorus atom in $PCl_3$ and $PF_3$ as 8 and 5·6, respectively, and percentage ionic character in $PF_3$ as 65. Molar polarization ($P_M$ c.c.) in carbon tetrachloride and benzene between −25° and 40°C. is given as:

| | Carbon tetrachloride | | | Benzene | | | Ref. |
|---|---|---|---|---|---|---|---|
| | −25° | 0° | +25° | 10° | 25° | 40° | |
| $PCl_3$ | — | — | — | — | 54 | 53·2 | 50 |
| $PCl_3$ | 43·8 | 42·2 | 42·2 | 48·2 | 46·8 | 45·6 | 49 |
| $PBr_3$ | 47·4 | 46·5 | 45·8 | 43·0 | 41·5 | 40·5 | |

Measurements in the vapour state (up to 463°K.) show deviations from linearity in the plot of $P_M$ against $1/T$; the explanation offered[53] is of two separate moments corresponding to different internal energy levels. Values of electron polarization ($P_E$) in carbon tetrachloride solution are $PCl_3$ 28·64, $PBr_3$ 39·02, giving interatomic distances, calculated from $(P_E/4\pi N)^{1/3}$, in general agreement with those derived from other sources.[54] The infra-red and Raman spectra of phosphorus(III) chloride have been described.[493, 497] Molecular data for phosphorus(III) chloride are listed in Table II, page 441; other useful references[55–8] include information on bond angles and lengths, and stereochemistry. A recent electron diffraction study in the vapour state at 300° and 500°K.[59–61] has shown a significant increase in P–Cl and Cl–Cl distances (0·3 and 0·4% respectively) and of associated mean amplitudes (19 and 31%, respectively) at the higher temperature. By using the mean square amplitudes of vibration in conjunction with the accepted vibration frequencies, force constants for the $PCl_3$ molecule (cf. Table III, page 441) have been evaluated as follows: $f_d$ 2·82 ± 0·37, $f_{dd}$ 0·58 ± 0·29, $f_\alpha$ 0·27 ± 0·03, $f_{\alpha\alpha}$ 0·045 ± 0·03, $f_{d\alpha}$ 0·27 ± 0·21, $f_{d\alpha'}$ 0·07 ± 0·28. Summation of the characteristic volumes for bound atoms (derived from $v_{\text{minimum}}$, $v_{\text{covalent}}$ and the number of bonds of a given type) gives[62] values of 82·70, 96·05 and $120{\cdot}86 \times 10^{-24}$ c.c. for the $PCl_3$, $PBr_3$ and $P(C_2H_5)_3$ molecules, respectively. The first-order centrifugal distortion constants of phosphorus(III) chloride have been calculated from the microwave rotational spectra. They are $D_J = 1{\cdot}7$, $D_{JK} = -1{\cdot}879$ kMc.[498] The measured molar diamagnetic susceptibility $-\chi_m \times 10^6$ for phosphorus trichloride was 66·0[63] or 63·4[64] c.g.s. units; the diamagnetic anomaly (6·3 c.g.s. units), i.e. the difference between calculated and observed values, was related[64] to structural constraint.

The mass spectrum at 120 e.v. showed the presence of $PCl_3^+$, $PCl_2^+$, $PCl^+$, $P^+$, $PCl_2^{++}$, $PCl^{++}$, $P^{++}$ and $Cl^+$ ions.[65] At 70 e.v. the relative abundances, appearance potentials, probable processes and heats of formation for the principal positive ions are given[7] as:

| Ion | $m/e$ | Relative abundance | Appearance potential (e.v.) | Process | $\Delta H_f^+$ kcal. mole$^{-1}$ |
|---|---|---|---|---|---|
| $PCl_3^+$ | 138 | 31·5 | 10·7 | $PCl_3 \rightarrow PCl_3^+$ | 175 |
| | 136 | 30·8 | | | |
| $PCl_2^+$ | 101 | 100·0 | 12·3 | $\rightarrow PCl_2^+ + Cl$ | 182 |
| $PCl^+$ | 66 | 29·2 | 16·8 | $\rightarrow PCl^+ + 2Cl$ | 257 |
| $Cl^+$ | 35 | 48·3 | 20·2 | $\rightarrow Cl^+ + P + Cl_2$ | 317 |
| $P^+$ | 31 | 20·9 | 21·2 | $\rightarrow P^+ + 3Cl$ | 329 |

$^{31}P$ nuclear magnetic resonance shifts (p.p.m.) for the phosphorus trihalides referred to 85% phosphoric acid are given[66] as:

| | | | |
|---|---|---|---|
| $PF_3$ | −97 | $POClF_2$ | −14·8 |
| $PI_3$ | −178 ($P_2I_4$ in $CS_2$ −170) | $POCl_2F$ | 0·0 |
| $PCl_3$ | −215 | $POCl_3$ | −5·4 |
| $PBr_3$ | −222 | $PSCl_3$ | −30·8 |

The chemical shifts of the following mixed halide-pseudohalides have been measured: $PX_{3-n}(NCO)_n$, X = F, Cl, Br; $PX_{3-n}(NCS)_n$, X = Cl, Br; $OPCl_{3-n}(NCS)_n$, and $SPCl_{3-n}(NCS)_n$ ($n = 0$–3). The increments in the $^{31}P$ chemical shift for 3-coordinate phosphorus compounds are −32 p.p.m. for NCO and −29 p.p.m. for NCS. Except in the PF compounds in which strong P–F ($\pi$) bonding occurs, the chemical shifts can be accurately predicted from these increments. For the 4-coordinate compounds, where only electronegativity differences are responsible for the alteration of the chemical shift, the corresponding increments are +13 and +21 p.p.m. Hence the electronegativity of the ligands decreases in the series Cl > NCO > NCS > Br.[501]

Viscosity/temperature data[67–9] for phosphorus(III) chloride, bromide and phosphoryl chloride conform to the Bachinskii[70] formula $\eta_{(\text{poise})} = C/(v - \omega)$, where $v$ is the specific volume, and $C$ and $\omega$ are characteristic constants with the values:

| | Temperature | $C$ | $\omega$ |
|---|---|---|---|
| $PCl_3$ | −15 to +70°C. | 0·000852 | 0·5029 |
| $PBr_3$ | −15 to +60°C. | 0·000521 | 0·3205 |
| $POCl_3$ | 2 to 80°C. | 0·000712 | 0·5352 |

Other data for phosphorus(III) chloride[72] were found to conform less closely to the Andrade[71] formula, $\eta_{(\text{poise})} = Av^{-1/3} \exp\{c/vT\}$ where $A$ and $c$ are arbitrary constants, than did those for phosphoryl chloride and for normal liquids.

| | Temperature | *A* | *c* |
|---|---|---|---|
| $PCl_3$ | 0 to 50°C. | 0·001830 | 163 |
| $POCl_3$ | 0 to 80°C. | 0·0005014 | 506 |

The deviation is indicative of change in associative tendency with temperature.[72] Later values for the viscosity of phosphorus(III) chloride between −65·1 and +60·1°C. were in reasonable agreement with the data of Bowden and Morgan,[72] the logarithm of the viscosity being inversely proportional to temperature over the whole range.[323] Density, $d_4^t$ from 0° to 76°C., is given by: $1{\cdot}6128-1{\cdot}869\times10^{-3}t+1{\cdot}84\times10^{-7}t^2-7{\cdot}92{\cdot}10^{-9}t^3$ [73–4] and derived values together with viscosity–temperature data are summarized in Table II. Later authors give the equation:

$$p_{PCl_3} = 1{\cdot}6095-1{\cdot}762\times10^{-3}t-1{\cdot}51\times10^{-6}t^2$$

for the density of phosphorus(III) chloride over the temperature range 0–115°C. They found a critical temperature of 290·0°C. and a critical density 0·520 g./c.c.,[500] in good agreement with earlier values.

*Table II.—Density (g./c.c.) and Viscosity (poise) Data for Phosphorus(III) Chloride*

| Ref. | 73, 74 | 67–69 | 72 | |
|---|---|---|---|---|
| °C. | $d_4^t$ | $\eta$ | $\eta_{\text{observed}}$ | % deviation (obs.–calc.) |
| 0 | 1·6128 | 0·00755 | 0·00656 | +14·3 |
| 15 | 1·5848 | 0·00661 | 0·00560 | +6·6 |
| 25 | 1·5661 | 0·00616 | 0·00501 | +0·2 |
| 35 | 1·5473 | 0·00584 | 0·00479 | −0·2 |
| 50 | 1·5188 | 0·00548 | 0·00453 | Nil |
| 70 | 1·4802 | 0·00508 | — | — |
| b.p. °C. | 75·95 | — | 75·7 (758 mm.) | |

Cryoscopy in nitrobenzene[75] gave association factors for phosphorus(III) chloride and phosphoryl chloride of 1·09 and 1·08, respectively (cf.[76] where normal freezing point lowering was observed for phosphorus(III) chloride in benzene). Viscosity isotherms between 0° and 30°C. indicate ideality for each of the phosphorus(III) chloride–diethyl ether,[77] –benzene and –nitrobenzene[78] systems; parachors for the phosphorus trichloride–benzene system agree with values calculated from $[P]=(1-x)[P]_1+x[P]_2$, where $x$ is the mole fraction of solute with parachor value $[P]_2$.[79] Linear relationships have been demonstrated between the surface tension of the $PX_3$ halides at 75°C., the covalent radius of the halogen atom[80–2] and the energy of the P–X bond,[83] where X is chlorine, bromine or iodine.

*Table III.—Molecular Properties Derived[84] from Ultrasonic Measurements*

| Halide | Molar sound velocity | $K_{\text{ad.}}$ | $K_{\text{is.}}$ | $C_p/C_v$ | Thermal pressure coefficient dyne cm.$^{-2}$ deg.$^{-1}$ | Energy volume coefficient dyne cm.$^{-2}$ |
|---|---|---|---|---|---|---|
| | | ($10^{-12}$ cm.$^2$ dyne$^{-1}$) | | | | |
| $PCl_3$ | 831·3 | 72·07 | 104·4 | 1·45 | $11{\cdot}56\times10^6$ | $3504\times10^6$ |
| $PBr_3$ | 922·4 | 41·74 | — | — | — | — |
| $POCl_3$ | 916·5 | 64·26 | — | — | — | — |

Ultrasonic measurements[84] gave the sound velocity ($v$) in phosphorus(III) chloride, bromide and phosphoryl chloride at 30°C. as 944·1, 916·7 and 969·3 m. sec.$^{-1}$, respectively. Derived values for molar sound velocity $[(M/d)\times v^{1/3}]$ and adiabatic compressibility ($K_{ad.} = 1/v^2d$) are listed in Table III, as are values for isothermal compressibility ($K_{is.} = K_{ad.} + T\alpha^2/C_p.d$), specific heat ratio ($C_p/C_v$), thermal pressure coefficient $(\delta P/\delta T)_v$ and energy–volume coefficient $(\delta E/\delta V)_T$ for phosphorus trichloride, calculated[84] from $v$, and available data for coefficient of thermal expansion ($\alpha$) and heat capacity ($C_p$).

### ISOTOPE EXCHANGE

Halogen exchange between radiochlorine and phosphorus(III) or (V) chlorides, and between radiobromine and phosphorus(III) bromide, each in carbon tetrachloride solution at 23°C., was complete in less than 3 min.[85] In contrast, exchange of phosphorus with phosphorus(III) chloride in carbon disulphide solution was approximately 4% in a few minutes and 30% in a few days.[86] In chloroform solution at 20°C. under strictly anhydrous conditions, halogen exchange between $^{36}$Cl-pyridinium chloride and phosphorus(III) chloride at 20°C. was again complete in less than 3 min.[87] Halogen exchange between $^{35}$Cl-labelled hydrogen chloride and phosphorus(III) chloride in the vapour phase at 20°C. was complete in 45 min. but with phosphoryl chloride it appeared to take much longer.[88] Exchange between $^{32}$P- or $^{36}$Cl-labelled phosphorus trichloride and phosphorus pentachloride in carbon tetrachloride solution indicates[89] equal reaction rates for both phosphorus and chlorine. The reaction is of first order in $PCl_5$ ($k \times 10^3$ hr.$^{-1} = 0{\cdot}90 \pm 0{\cdot}08$ at 0·1°, $10{\cdot}6 \pm 1{\cdot}4$ at 25°, $82 \pm 6$ at 50°C., activation energy $15{\cdot}9 \pm 0{\cdot}1$ kcal. mole$^{-1}$) and of zero order in $PCl_3$.

### REORGANIZATION IN THE PHOSPHORUS TRIHALIDES

Nuclear magnetic resonance methods following complete equilibration of $P(OPh)_3$–$PCl_3$, $P(OPh)_3$–$PBr_3$ and $P(OPh)_3$–$PCl_3$–$PBr_3$ mixtures in sealed tubes at 180°C. have indicated[90] higher concentrations of phosphorus(III) mixed compounds (type $PCl(OPh)_2$,$PCl_2.OPh$, etc.) than would be predicted on a statistical basis for truly random processes (Ph = phenyl). Except for the relatively unstable $PClBr_2$, equilibrium constants of formation and free energy values calculated from the experimental data demonstrated the higher stability of the mixed compounds. It was concluded that ligand exchange was considerably faster and deviations from the theoretical random distribution more pronounced than those which occur with the same ligands in the phosphoryl or thiophosphoryl systems, i.e. systems based on the quadruply connected P-atom.[90–2] Enthalpy, free energy and entropy functions have been calculated for $PCl_2Br$ and $PClBr_2$ over the temperature range 298·2–1000°K.[516]

Phosphorus trichloride vapour sorption on activated sugar charcoal was represented[93] by: $a_{(\text{mg. }PCl_3/\text{g. charcoal})} = xp^n$, where $p$ = equilibrium pressure in cm. and $x$ and $n$ = 22·945 and 0·2255 at 20°, 16·260 and 0·2540 at 30° and 6·427 and 0·3300 at 50°C. respectively.

## Chemical Properties

### REDUCTION AND OXIDATION

Phosphorus trichloride, tribromide and phosphoryl chloride undergo gas-phase reduction with hydrogen under electrodeless electric discharge giving small yields of red and yellow phosphorus and of incompletely identified liquid products.[1, 5] By subjecting a phosphorus trichloride–hydrogen gas stream (mole ratio = 2:1) at −78°C. and 19 mm. pressure to continuous electric discharge at 7500 v. between molybdenum electrodes, maximum yields of phosphorus dichloride (= 3·5 g./hr.) were obtained.[6] Organic phosphoryl chlorides, $RPOCl_2$, are formed when a slow stream of a paraffin hydrocarbon and oxygen is passed through phosphorus trichloride at 60°C.[94]; sulphuric acid and iodine behave as inhibitors. The analogous reaction fails to occur with phosphorus tribromide. On passing dry oxygen into rapidly stirred phosphorus(III) chloride–*cyclo*hexane mixtures at 20°C. or below, up to 30% conversion to *cyclo*hexyl phosphoryl chloride was obtained under optimum conditions.[95–6] There was no change in yield over the temperature range −40° to +70°C. and the speed of the reaction appeared to be governed only by the rate of dissolution of oxygen in the mixture. From a recent study[97] it is deduced that the reaction proceeds by a free radical chain mechanism in which Cl atoms participate as one chain carrier. When hydrogen plus oxygen was passed through phosphorus(III) chloride the only certain products of the resulting exothermic reaction were phosphoryl chloride and 'phosphorus suboxide' $P_4O$.[98] The reaction between gaseous oxygen and liquid phosphorus(III) chloride to give phosphoryl chloride is of commercial importance (page 487) and a kinetic study[99] has shown it to be initially heterogeneous, with dissolution of oxygen the rate-determining step. The energy of activation is small and a free radical mechanism involving the $Cl_3\overset{+}{P}O\overset{-}{O}$ biradical was proposed. Phosphorus(III) chloride was found to be the most readily oxidized by dimethyl sulphoxide of a series of P(III) compounds. This is presumably because the chlorine atoms confer strong acceptor properties on the phosphorus atom, favouring electrophilic attack on the oxygen atom of the sulphoxide.[502]

HYDROLYSIS

Aqueous hydrolysis of phosphorus trichloride gave solutions for which surface tension and pH measurements at 20°C. changed with concentration and time and tended towards limiting values.[100] The facts were said to be in agreement with the presence of two forms of phosphorous acid in equilibrium. Mild oxidants were said[101] to convert α- and β-phosphorous acids to hypophosphoric and phosphoric acids, respectively:

$$2P(OH)_3 \xrightarrow[+O]{} (HO)_2PO.PO(OH)_2 + H_2O;\ HPO(OH)_2 \xrightarrow[+O]{} H_3PO_4$$

(but see Section XXI). The existence of hydrolysis products stable in neutral solution and resistant to iodine was reported.[102] Chromatographic and iodimetric analyses following hydrolysis of phosphorus(III) chloride, bromide or iodide in buffered or alkaline solution at 0°C. led[103] to the identification of a number of phosphorus oxyacids in the form of their sodium salts, including:

| | | |
|---|---|---|
| (i) | pyrophosphite | $(NaO)HPO.OPO.H(ONa)$ |
| (ii) | phosphite | $HPO(ONa)_2$ |
| (iii) | diphosphite | $(NaO)HPO.PO(ONa)_2$ |
| (iv) | hypophosphate | $(NaO)HOPO.PO(ONa)_2$ |
| (v) | phosphate | $HOPO(ONa)_2$ |
| (vi) | pyrophosphate | $(NaO)HOPO.OPO.OH(ONa)$ |
| (vii) | *iso*hypophosphate | $(NaO)HPO.OPO(ONa)_2$ |
| (viii) | unidentified salt, believed to contain 3 or 4 P atoms and both P–O–P and P–P linkages. Gives (iv) and (vii) by acid hydrolysis | |

Under mild conditions phosphorus trichloride gives (i) and (ii) together with small amounts of (iii) to (vii); at increased alkalinity the products were (ii) with much less (i) and increased amounts of (iii) to (vii). Phosphorus tribromide gave some phosphine and approximately equal amounts of (ii) to (v), (vii) and (viii); phosphorus tri-iodide gave mainly phosphine, (iv) and (viii), some (iii), (v) and (vii) and a little (ii) and (vi). Thus the tendency to form P–P bonded compounds increases on passing from phosphorus(III) chloride to the less polar iodide. Similar results were obtained from the hydrolysis of a series of P(III) halides and pseudohalides. The hydrolysis was carried out by 5N NaOH at 0°C. under nitrogen, with a molar ratio $PX_3 : NaOH = 1:7$. The relative molar percentages of various phosphorus oxyanions formed were as follows[503]:

| Species | $PCl_3$ | $PBr_3$ | $PI_3$ | $P(NCO)_3$ | $P(NCS)_3$ | $P(CN)_3$ |
|---|---|---|---|---|---|---|
| $P^1$ | — | 1·3 | 0·9 | 10·6 | — | 3·7 |
| $P^3$ | 84·3 | 41·9 | 42·3 | 84·7 | 92·5 | 79·0 |
| $P^5$ | 6·1 | 8·9 | 18·6 | — | — | — |
| $P^2$–$P^4$ | 4·9 | 17·1 | 3·6 | 3·8 | 3·3 | 3·8 |
| $P^4$–$P^4$ | 2·4 | 5·9 | 4·6 | — | 0·1 | — |
| $P^3$–O–$P^5$ | — | — | 3·6 | — | — | † |
| $P^5$–O–$P^5$ | — | — | 1·6 | — | — | — |
| Anions cont. >2P atoms* | 2·9 | 23·8 | 24·7 | 1·0 | 3·2 | 4·2 |

* Some isohypophosphate detected, but contaminated with an unidentified species.
† $P^4$–$P^3$–$P^4$ was identified in every case. No detectable amount of phosphine was formed.

The preparation and properties of reduced phosphorus acids and their salts are discussed in Sections XX to XXII, but those reactions which involve controlled hydrolysis of phosphorus(III) halides are summarized in Table IV. In this Table use is made of a systematic skeletal nomenclature[104] based on the assignment of an oxidation number to each phosphorus atom.

*Table IV.—Preparation of Reduced P-acids by the Controlled Hydrolysis of Phosphorus(III) Halides*

| Preparation recipe | Product | | Ref. |
|---|---|---|---|
| | Systematic designation of the acid | Common name, empirical formula, yield | |
| Stir 1 mole $PCl_3$ with 5 moles crystalline $H_3PO_3$ at 35°C. for 5 hr. Then keep under vacuum over KOH and $P_2O_5$. | $P^3$–O–$P^3$ | pyrophosphorous acid $H_4P_2O_5$ (i) | 105<br>106 |
| Add $PCl_3$ to 80 to 98% $H_3PO_3$ at 85° to 90°C. in a counter-current process. | $P^3$ | phosphorous acid $H_3PO_3$ (ii) (100% conversion) | 107 |
| Add 1 mole $PBr_3$ to 4 moles $NaHCO_3$ in 200 ml. water with stirring at 0° to 5°C.* | $P^2$–$P^4$ | trisodium diphosphite $Na_3HP_2O_5,12H_2O$ (iii) (45 g.) | 108 |
| Add 1 mole $PCl_3$ to 1/3 mole $NaH_2PO_4$+2/3 mole $Na_2HPO_4$ in 600 ml. water with stirring at 0°C.* | $P^3$–O–$P^5$ | trisodium isohypophosphate $Na_3HP_2O_6,8H_2O$ (vii) (50 g.) | 109<br>110 |
| Add $PCl_3$ to bromine water at 0°C.* | $P^4$–$P^3$–$P^4$ | $Na_5P_3O_8,14H_2O$ | 111 |

* For subsequent separative procedures, see reference.

When progressive increments of water were added to ethereal solutions of phosphorus trichloride, the plot of temperature rise against water added showed breaks at 1, 2 and 3 moles $H_2O$/mole $PCl_3$ in accord with the probable formation of intermediate mono- and dichlorophosphorous acids[112] (see Section XXXI). Other workers[98] found no evidence for the formation of chlorophosphorous acids, either in reactions with free or salt-hydrate water carried out in various solvents between −70° and −20°C. The only identifiable products were phosphorous and hypophosphorous acids, phosphoryl chloride and a phosphorus suboxide, $P_4O$. However, a detailed study[504] of the reaction between phosphorus(III) chloride and phosphorous acid showed that, although reversible, it could be made to give very high yields of pyrophosphorous acid, $H_4P_2O_5$, because of the sparing solubility of hydrogen chloride in the reactants. No vapour phase reaction between phosphorus trichloride and water was observed at 25° to 200°C.[113] But for phosphoryl chloride, hydrolysis was found to proceed at a rate proportional to the absorption of water vapour by the phosphoric acid deposited on the walls of the containing vessel. At higher temperatures no reaction occurred.

### REACTIONS WITH SULPHUR AND SULPHUR COMPOUNDS

The addition reaction of sulphur with phosphorus (III) chloride to give thiophosphoryl chloride goes to completion in 2 to 5 hr. at 150° to 160°C. in the presence of 1% of alkali or alkaline earth sulphide catalyst.[114] Commencing with a mixture of sulphur (14), phosphorus trichloride (40), thiophosphoryl chloride (44 wt. %) containing 2 wt. % of carbon activated with potassium sulphide, the reaction is said to be complete (accompanied by a temperature rise to 125°C.) after approximately 3 hr. boiling under reflux.[115] Sulphur monochloride can also be used as a catalyst.[116] With sulphur trioxide[117] and hydrogen disulphide[118] the respective reactions are given as:

$$PCl_3 + SO_3 \rightarrow POCl_3 + SO_2$$
$$3PCl_3 + 3H_2S_2 \rightarrow PSCl_3 + P_2S_5 + 6HCl$$

Phosphorus(III) chloride is miscible in all proportions with liquid sulphur dioxide[119] and liquid carbon dioxide.[120] The former solutions show amphoteric property, and with the $SO_2$-base tetraethylammonium sulphite deposit phosphorus trioxide, soluble in excess of the reagent.[121] With potassium fluoride in liquid sulphur dioxide, phosphorus trifluoride is formed.[122] Sulphur nitride in benzene solution reacts with thionyl chloride in phosphorus(III) chloride on vigorous agitation to give phosphonitrilic chloride, $(PNCl_2)_3$. The latter crystallizes on the walls of the vessel after standing and may be separated by sublimation *in vacuo*.[123] Sulphur nitride dissolves in excess of phosphorus trichloride with formation of a white precipitate having the composition $P_2NCl_7$. This compound was also obtained by heating phosphonitrilic chloride trimer with phosphorus pentachloride (mole ratio 1:3) in phosphoryl chloride as solvent in a sealed tube at 250°C.[124] Infra-red analysis after recrystallization from chloroform at −55°C. indicated a $NPCl_2,PCl_5$ structure. Cryoscopy and $^{31}P$ nuclear magnetic resonance spectroscopy on 0·02 M. solutions in nitrobenzene showed 95% dissociation to $PCl_4^+$ and $NPCl_3^-$ ions.[125]

### REACTIONS WITH HALOGENS AND HALOGEN COMPOUNDS

Phosphorus trichloride reacts with fluorine in the vapour phase to give appreciable yields of 'salt-form' tetrachlorophosphonium hexafluorophosphate $[PCl_4^+][PF_6^-]$ together with molecular tetrachlorofluorophosphorane $PCl_4F$.[126] The reactions with chlorine to give phosphorus pentachloride and with bromine to give a complicated series of phosphorus bromochlorides are discussed on pages 476 and 486–7. Phosphorus trichloride is slightly soluble in molten iodine, but no compounds are formed.[127–8] However, the transient formation of $PCl_3I_2$ may be responsible for the acetyl iodide and hydrogen iodide formed when acetic acid is treated with a mixture of phosphorus(III) chloride and iodine.[505] Fluorination giving phosphorus(III) fluoride and mixed chlorofluorides occurs with antimony, calcium[129] and ammonium[130] fluorides, while mixtures of phosphorus(III) halides in the liquid phase undergo reorganization to mixed halides at room temperature.[131–5] With tetrachloroantimony(V) fluoride vigorous fluorination occurs; phosphorus(III) fluoride is formed and white tetrachlorophosphonium hexachloroantimonate $[PCl_4^+][SbCl_6^-]$ is precipitated,[136] the latter giving conducting solutions in acetonitrile. The reaction: $PCl_3 + 3ICl = [PCl_4^+][ICl_2^-] + I_2$ occurs on addition of phosphorus trichloride to iodine chloride and is strongly exothermic. The resulting solutions have high electrical conductivities (max. = 0·037 mho cm.$^{-1}$ at 6·8 mole % $PCl_3$ and 45°C.) and the product (identical with that from $PCl_5 + ICl$) can be isolated following repeated extraction with carbon tetrachloride.[137]

REACTIONS WITH NITROGEN-CONTAINING COMPOUNDS

The principal products of reaction with nitrogen tetroxide at $-10°C.$ are phosphoryl, pyro- and tetraphosphoryl chlorides, a crystalline compound of composition $P_2O_6NCl_2$, nitric oxide, nitrogen trioxide and nitrosyl chloride[138] (but see pages 506–7). With liquid ammonia, the phosphorus triamide first formed undergoes thermal decomposition with loss of ammonia and hydrogen to give phosphorus pernitride[139]:

$$\begin{array}{ccccc} P(NH_2)_3 & \xrightarrow[0°C.]{} & P_2(NH)_3 & \longrightarrow & P_4N_6 \\ \text{amide} & & \text{imide} & & \text{pernitride} \end{array}$$

With nitryl chloride an exothermic oxidation reaction occurs, the products being phosphorus pentachloride, phosphoryl chloride, nitrosyl chloride and nitrogen tetroxide.[140] Heating phosphorus(III) chloride with silver cyanide at 100°C. for 24 hr. and then at 130° to 150° *in vacuo* for 2 days, gave[141] a white needle sublimate of phosphorus tricyanide, readily hydrolyzed by water and reacting with dicyanogen under pressure to form the pentacyanide. Reaction with mercurous thiocyanate, silver *iso*cyanate or silver thiocyanate in benzene or carbon disulphide solution followed by careful fractionation at reduced pressures has led[141–4] to the isolation of a number of phosphorus(III) compounds containing pseudo-halogen. Phosphorus trithiocyanate ($\text{b.p.}_{(16\ \text{mm.})} = 164°C.$) and the black solid polymer formed at 170°C were described by earlier workers.[145–6] The chief physical properties of the newer compounds are:

| | m.p. °C. | b.p. °C. | $d_4^{20}$ g. c.c.$^{-1}$ | Refractive index | $\log_{10} p_{\text{mm.}}$ | Ref. |
|---|---|---|---|---|---|---|
| $P(NCO)_3$ | $-2\pm0{\cdot}5$ | $169{\cdot}3\pm0{\cdot}3$ | 1·439 | 1·5352 | $8{\cdot}7455–2595/T$ | 142 |
| $PCl(NCO)_2$ | $-50\pm2$ | $134{\cdot}6\pm1$ | 1·505 | — | $8{\cdot}880–2445/T$ | 144 |
| $PCl_2(NCO)$ | $-99\pm2$ | $104{\cdot}4\pm0{\cdot}5$ | 1·513 (31°C.) | — | — | 143 |
| $PCl_2(SCN)$ | $-76$ | 148 | 1·546 | — | $9{\cdot}427–2757/T$<br>(30–54 mm.) | 144 |

The mixed compounds undergo appreciable rearrangement at elevated temperatures, e.g., the reaction $3PCl_2(SCN) \rightarrow 2PCl_3 + P(SCN)_3$ proceeds at approximately 1% per hr. at 80°C. or 1% per min. at 148°C. while analogous rearrangement of the monochloro-compound, $PCl(SCN)_2$, appeared[143] to be sufficiently rapid to prevent its isolation. Exchange of pseudo-halogen for halogen readily occurs where conditions permit elimination of a more volatile compound,[147–8], e.g. by heating:

$$\begin{array}{r} P(NCO)_3 + 3PhCOCl \rightarrow PCl_2NCO \\ P(NCO)_3 + 2HgCl_2 \rightarrow PCl_2NCO \\ P(NCO)_3 + 2AlCl_3 \rightarrow PCl_3 \\ PO(NCS)_3 + 3HgCl_2 \rightarrow POCl_3 \end{array}$$

Sulphonation to the corresponding thiophosphoryl compound,[149] or fluorination to mixed phosphorus(III) fluoro compounds[150] also occurs:

$$\left.\begin{array}{c} P(NCO)_3 + S \text{ in sealed tube at} \\ 140°C. \end{array}\right\} \rightarrow PS(NCO)_3 \qquad \text{b.p., } 215°C.$$

$$P(NCO)_3 + SbF_3 \xrightarrow[\text{at } 36°–90°C.]{} \left\{\begin{array}{l} PF(NCO)_2 \\ PF_2NCO \end{array}\right. \qquad \begin{array}{l} \text{b.p., } 98{\cdot}7\pm0{\cdot}3°C. \\ \text{b.p., } 12{\cdot}3\pm1°C. \end{array}$$

$$P(NCS)_3 + SbF_3 \xrightarrow[\text{at } 150°–200°C.]{} PF_2NCS \qquad \text{b.p., } 90{\cdot}3\pm0{\cdot}3°C.$$

COMPLEX FORMATION

The phosphorus(III) halides may be expected (see under phosphorus trifluoride, page 444) to show an increasing electron donor activity towards acceptor molecules, and a decreasing electron acceptor behaviour in $\pi$ bond formation by *d*-orbitals, proportional to the reduction in halogen electronegativity which occurs on passing from fluoride to chloride, bromide and iodide. For the typically electron acceptor boron halides, complex compounds with phosphorus(III) chloride have been reported as follows:

$PCl_3,BF_3$ formed as white crystals below $-12$°C., decomposes at $-6$°C.[151]
$PCl_3,BCl_3$ formed as white crystals below $-10$°C., sublimes *in vacuo*, and is vigorously hydrolyzed.[152]
$PCl_3,BBr_3$, m.p. 42°C., dissociates to liquid $PCl_3$ + gaseous $BBr_3$ after 3 days *in vacuo*, and is vigorously hydrolyzed[153–4, 506] (cf. $PBr_3,BBr_3$, m.p. 61°C. stable *in vacuo* at room temperature).
$PCl_3,BI_3$, yellowish white crystals, formed in $CS_2$ at $-40$°C., decomposes at 35°C.[506]

In the case of $PCl_3,BI_3$ and $PCl_3,BBr_3$ ligand interchange is said to occur, with evolution of $BCl_3$, at 0° and 35°C., respectively.[506] Other addition complexes described in the literature include:

$(CuCl)_2,PCl_3$, dissociation pressure = 16, 47 and 170 mm. at 0, 20 and 50°C., respectively. With methanol, MeOH, gives $CuCl.P(OMe)_3$, m.p. 216° to 217°C.[155]
$GaCl_3,PCl_3$, m.p. 28°C. with decomposition. Heat of formation from its components at 25°C. = 3·4 kcal. $mole^{-1}$.[156]
$[RPCl_3]^+[AlCl_4]^-$ liquid or solid at ordinary temperatures depending on the nature of the alkyl group R. Formed by direct addition from equimolar alkyl, phosphorus(III) and aluminium chloride mixtures. Controlled hydrolysis gives alkyl phosphoryl dichlorides $RPOCl_2$; $H_2S$ gives alkylthiophosphoryl chlorides, $RPSCl_2$, then dithiophospho-alkanes, $RPS_2$. Reduction with powdered antimony gives alkylphosphonous-dichlorides, $R_2P_2Cl_2$.[157–9]
$CCl_4,PCl_3,AlCl_3$ from $CCl_4$–$PCl_3$–$AlCl_3$ mixtures after 4 hr. at 45° to 55°C. Forms $CCl_3POCl_2$ on hydrolysis.[160]

However, a recent vapour pressure/composition study,[154] using purified reagents in an all-glass high vacuum apparatus, failed to show any evidence of stable complex formation between phosphorus trichloride and either aluminium or gallium trichlorides, or boron trifluoride at $-78$°C., or boron trichloride at $-45$° and $+25$°C. A comparison of their boron trichloride adducts[154] shows phosphorus(III) chloride to be a much weaker Lewis base than either phosphine or trimethylphosphine thus:

$Me_3N,BCl_3$ undergoes negligible dissociation in the gas phase at 100°C.
$H_3P,BCl_3$ dissociates above 20°C.
$Cl_3P,BCl_3$ fails to associate down to $-78$°C.

With liquid diboron tetrachloride at low temperatures, the 1:2 complex $B_2Cl_4,2PCl_3$ is precipitated, m.p. $-16·3$° to $-15·8$°C., completely dissociated in the vapour phase but unchanged after 8 weeks in the dark at room temperature.[161] Phosphorus(III) chloride reacts with trimethylarsine at $-29·5$°C. giving white solid $Me_3As,PCl_3$, decomp. 0°C.; with trimethylstibine reduction to $Me_3SbCl_2$ and elemental phosphorus occurs.[162] Trimethylphosphine at 0°C. gives the 2:1 complex $(Me_3P)_2,PCl_3$[163] while with trimethylamine at $-78$° to 0°C. white solid $Me_3N,PCl_3$ is formed, m.p. 0°C., heat of dissociation $Me_3N,PCl_3(s) \rightarrow Me_3N(g) + PCl_3(g) = 22·4$ kcal. $mole^{-1}$.[164] In these compounds phosphorus(III) chloride appears to behave as an electron acceptor and thus in the Lewis sense is amphoteric.[154] The P–N bond energies for $Me_3N,PCl_3$ and $Me_3N,PBr_3$ are estimated at 6·4 and 3·1 kcal. $mole^{-1}$, respectively, indicating that either the greater electronegativity of chlorine increases the bonding or the greater steric effect of the bromine atom reduces it.[165] For $Me_3N,PMeCl_2$ the energy of complexing is estimated[166] as 2·9 kcal. $mole^{-1}$. The existence of white solid $F_3P,NMe_3$ at temperatures below its melting point is also confirmed, but to date there is insufficient evidence to decide whether the $PF_3$ molecule is a stronger acceptor than $PCl_3$ in these compounds. Phosphorus(III) chloride behaves as a typically $\pi$-bonding ligand in replacing the carbon monoxide from dimeric platinum carbonyl chloride, $[PtCl_2CO]_2$, even at low temperatures.[167] Direct action with nickel carbonyl in the liquid phase gives tetrakistrichlorophosphine nickel, $Ni(PCl_3)_4$, which separates as thermochromic crystals (pale yellow up to 120°C., white on cooling to $-30$°C.), following distillation of excess phosphorus(III) chloride and recrystallization from *n*-pentane.[168] Cryoscopy in benzene confirms the monomeric formula while magnetic susceptibility indicates the absence of unpaired electrons. When heated with phosphorus(III) fluoride $Ni(PCl_3)_4$ undergoes ligand exchange with formation of $Ni(PF_3)_4$. Thermal decomposition of $Ni(PCl_3)_4$ occurs with evolution of phosphorus(III) chloride and nickel(II) chloride, and formation of a mixture of heptanickel triphosphide and dinickel phosphide.[507] The products of reaction between phosphorus trichloride and cobalt carbonyl in benzene could not be characterized.[169]

## PHOSPHORUS(V) CHLORIDE

### Preparation

Phosphorus pentachloride is obtained commercially as a fine crystalline powder by addition of dry chlorine to approximately equal volumes of phosphorus trichloride and carbon tetrachloride contained in a stirred, lead-lined reaction vessel fitted with cooling water jacket and reflux condenser.[27, 29] Chlorination in phosphoryl chloride medium has also been described.[170] In either case the product is separated by filtration and the filtrate recycled. The direct reaction between phosphorus trichloride and chlorine gas has been used commercially[28, 171–2] and is also prescribed for laboratory synthesis of the pure material.[173–4] Other methods include passing chlorine gas into a suspension of red phosphorus in carbon tetrachloride[175] (a laboratory process), chlorine on aluminium phosphate,[176] the action of liquid chlorine upon phosphorus trichloride[177] and the reaction between phosphoryl chloride, carbonyl chloride and carbon at 400°C.[8]

### Physical Properties

In the liquid state or in solution in non-polar solvents, Raman spectrographic methods have shown all the P–Cl bonds in phosphorus(V) chloride to be alike; in the solid state however, the molecule is unsymmetrical and ionic.[178–82] Electron diffraction measurements for the vapour at 100°C.[183–4] indicated a trigonal bipyramidal structure with two P–Cl distances, viz.: 2·19 and 2·04 A., corresponding to apical and planar chlorine atoms, respectively. A complete vibrational assignment was made[185] based on $D_{3h}$ symmetry, the infra-red spectra for the vapour and solution in carbon-disulphide, and on the Raman spectrum for the solution in benzene. Conversely, normal co-ordinate analysis by the Urey–Bradley field, with introduction of an angle–angle interaction force, gave good agreement between calculated and observed infra-red and Raman frequencies.[508] Force constant data, in $10^5$ dynes cm.$^{-1}$, viz.: $k_r$ 2·892, $k_{r'}$ 1·805, $k_\alpha$ 0·111, $k_\beta$ 0·449, $g_r$ 0·236 and $g_{r'}$ 1·440 were evaluated such that P–Cl bond lengths by Badger's rule[186] were in close agreement with those derived from the electron diffraction measurements.[183–4] Earlier data[187–8] for both the molecular and ionic forms had been based on Raman evidence alone; recent infra-red and Raman studies[189–91] have led to further modification of the vibrational assignments for molecular $PCl_5$ and for the $PCl_4^+$ ion. In this work, phosphorus(V) chloride was shown to be fully dissociated to unsolvated $PCl_4^+$ and $PCl_6^-$ ions at 1 w/v. % dilution in methyl cyanide.[189] The solid formed by vapour deposition at 90°K. had an infra-red spectrum identical with those for the vapour or solution in carbon disulphide, and changing in an irreversible manner to that of the ionic form on allowing the sample to warm up.[190] Later cryoscopic, spectroscopic and conductimetric studies of phosphorus(V) chloride in various solvents have shown that it is predominantly present as molecular $PCl_5$ in phosphoryl chloride, benzene, 1,2-dichloroethane and *cyclo*hexane. In acetonitrile it is partly dissociated to $PCl_4^+$ and

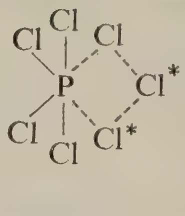
$PCl_6^-$ ions, while in carbon tetrachloride it appears to exist as a dimer, $P_2Cl_{10}$, of covalent structure.[509] *X*-Ray studies[192–3] showed crystalline phosphorus pentachloride to be tetragonal with $a = 9{\cdot}22$, $c = 7{\cdot}44$ A., 4 molecules per unit cell (density was 2·12 g./c.c.) and the space group *P*4/*n*. The arrangement of $PCl_4$ tetrahedra and $PCl_6$ octahedra was essentially of the cæsium chloride type, with P–Cl distance 1·97 A. in $[PCl_4]^+$ and 2·08 A. in $[PCl_6]^-$; the Cl–Cl distances ranged from 3·43 to 3·9, average 3·6 A. The constitutional change on melting is accompanied by an alteration in electrical properties,[194] viz.:

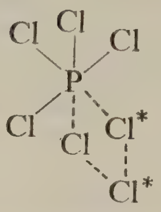
| | Specific conductance (mho cm.$^{-1}$) | Dielectric constant |
|---|---|---|
| $PCl_5$ crystals | $3{\cdot}3 \times 10^{-7}$ at 20°C. | — |
| | $3 \times 10^{-8}$ at 100°C. | 4·2 at 135°C. |
| $PCl_5$ liquid | $6 \times 10^{-9}$ at m.p. | 2·7 at 165°C.<br>(under pressure) |

and is reflected in the non-coincidence of the melting range (159° to 160·5°) crystallization point (157°) and halt in the temperature/time cooling curve (154° to 148°C. dependent on the cooling rate) observed[195] under sealed tube conditions. Dielectric constant measurements in carbon disulphide or carbon tetrachloride solution at 25°C. gave[196] molar polarization and molar refraction values (infinite dilution) of 51 and 35·5 c.c., respectively, and a dipole moment of 0·8 D. Phosphorus pentachloride behaves as an electrolyte in polar solvents and transport experiments[197] have supported the presence of $[PCl_4]^+$ and $[PCl_6]^-$ ions in solution. Equivalent conductance values in various solvents were:

| Solvent | Concentration moles $PCl_5$/litre | Equivalent conductance mho cm.$^2$ moles$^{-1}$ |
|---|---|---|
| Dioxan | 0·0825 | 0 |
| Diethyl ether | 0·05 | 0 |
| Phosphoryl chloride | 0·409 | 0·49 |
| Benzonitrile | 0·0301 | 1·03 |
| Benzoyl chloride | 0·0325 | 1·57 |
| Nitrobenzene | 0·0517 | 3·43 |
| Nitrobenzene | 0·0137 | 3·30 |
| Nitrobenzene | 0·00137 | 3·64 |
| Acetonitrile | 0·1870 | 26·3 |
| Acetonitrile | 0·0495 | 30·0 |
| Acetonitrile | 0·00554 | 34·5 |

Differences are attributed to the stabilization of the ionization by complex formation rather than to differences in dielectric constant of the medium. Cryoscopy in nitrobenzene showed negligible association to double molecules[197]; in carbon tetrachloride solution however, apparent molecular weight values of 259 and 473 at 0·0241 and 0·0959 M. concentrations, respectively, were obtained.[198] Chloride ion exchange in acetonitrile solution at 25°C. between $^{36}Cl$ labelled tetraethylammonium chloride and the tetrachlorophosphonium cation $[PCl_4]^+$ followed second-order kinetics with $k = 2{\cdot}00 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ and $t_{1/2}$ for 0·3 to 0·01 M. concentrations ranging from 1 to 19 min.; by contrast, $t_{1/2}$ for the exchange reaction with the hexachlorophosphonate anion $[PCl_6]^-$ was 0·6 sec. Conductimetry in acetonitrile solution confirmed that no such reaction as $[PCl_4]^+ + 2Cl^- = [PCl_6]^-$ occurs.[198] In carbon tetrachloride solution, three of the chlorine atoms in phosphorus pentachloride are much more rapidly exchanged for labelled molecular chlorine than the other two. Further, the formation reaction from phosphorus trichloride and chlorine, and the decomposition reaction with mercury, both in carbon tetrachloride media, were shown[199, 200] to proceed mainly through the equatorial positions. Differences in the two apical and three equatorial positions for trigonal bipyramidal molecules have been explained in terms of repulsion on the bonding pair,[126] of the maximum overlap principle,[510] or of differences in hybridization.[201–3] It is suggested[203] that hybridized *dp* bonds extend in the apical direction and $sp^2$ bonds extend in the equatorial direction. Possible intermediate states in the rapid exchange with chlorine ($Cl_2^*$) written:


(i)


(ii)

must lead[199, 200] either to no exchange, or (i) to exchange in the equatorial positions, (ii) to simultaneous exchange in both apical and equatorial positions. Steric hindrance should be no less at (ii) than at (i) and the experimental results therefore, were considered[199–200] to confirm a difference in bonding at the apical and equatorial positions. A study of overlap integrals for the *d*-orbitals in free atoms of P and S showed them too diffuse for useful contribution to bonding. For such molecules as $PCl_5$ and $SF_6$ a type of polarization was proposed[204–5] by which diffuse *d*-orbitals of the parent atom are sufficiently contracted to participate in $sp^3d$ and $sp^3d^2$ covalent bonding, respectively. On the basis of the cryoscopic evidence in carbon tetrachloride solution, it was suggested[198] that the observed[199–200] non-linear exchange rate with molecular chlorine may be due to simultaneous exchange reactions involving both simple and associated species. Mass spectroscopy at 50 e.v. gives peaks corresponding to: $P_2Cl_9^+$, $P_2Cl_7^+$, $P_2Cl_5^+$, $P_2Cl_3^+$, $P_2Cl_2^+$, $P_2Cl^+$ ion species as well as to a number of others containing one phosphorus atom. A solid–vapour equilibrium at the crystal surface, viz.: $[PCl_4]^+[PCl_6]^- \rightleftharpoons P_2Cl_{10}$, is proposed, wherein $P_2Cl_{10}$ molecules contain a 4-membered ring with two Cl-bridges involving $d_\pi$–$p_\pi$ bonding to two octahedrally connected phosphorus atoms. However, molecular weight determinations at relatively low temperatures provided no evidence of association in the vapour phase.[206–7]

Phosphorus(V) chloride sublimes at 159°C., 760 mm. pressure, and melts at 160°C. at slightly higher pressure or at 167°C. at 919 mm.[208] The vapour pressure of the solid from 100° to 159°C. is given by $\log_{10} p_{\text{mm.}} = 11{\cdot}034 – 3523/T$, where $T$ is in °K., and the density of the liquid from 162° to 190°C. is given by $d_4^t = 1{\cdot}599 - 0{\cdot}0019 (t - 160°\text{C.})$ with $t$ in °C. The heat of sublimation to equilibrium vapour composition is 16·1 kcal. mole$^{-1}$, and to undissociated $PCl_5$ molecules 15·5 kcal. mole$^{-1}$. Equilibrium constant values for the dissociation $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ between 422° and 502°K. are given by $\log_{10} K_{p(\text{mm.})} = 6{\cdot}66 + 1{\cdot}75 \log T – 4376/T$; the heat of dissociation at 200°C. is 22 kcal. mole$^{-1}$, and at 160°C., 760 mm., the vapour is 13% dissociated.[208] Experimentally determined thermal conductivities ($K$) for the dissociating vapour system at 145° to 175°C. at pressures below 1 atm. agreed well with the calculated values[209] thus:

| °C. | $P_{\text{total}}$ (mm. Hg) | $K_{\text{experimental}}$ (g.-cal. cm.$^{-1}$ | $K_{\text{calculated}}$ sec.$^{-1}$deg.$^{-1}$ × $10^5$) |
|---|---|---|---|
| 145 | 151·0 | 11·28 | 11·42 |
| | 248·0 | 9·64 | 9·75 |
| | 309·0 | 8·85 | 8·88 |
| | 315·0 | 8·86 | 8·83 |

| | | | |
|---|---|---|---|
| 160 | 164·5 | 14·04 | 14·31 |
| | 289·4 | 12·20 | 12·27 |
| | 350·3 | 11·60 | 11·53 |
| | 363·9 | 11·53 | 11·40 |
| 175 | 188·0 | 15·95 | 16·51 |
| | 333·0 | 14·75 | 14·67 |
| | 386·3 | 14·42 | 14·13 |
| | 422·5 | 13·92 | 13·79 |

Values of standard heat, free energy and equilibrium constant of formation at 298·15°K. are given[40–2] as:

| | crystals | vapour |
|---|---|---|
| $\Delta H_f^\circ$ | $-110{\cdot}7$ | $-95{\cdot}35$ kcal. mole$^{-1}$ |
| $\Delta G_f^\circ$ | — | $-77{\cdot}59$ kcal. mole$^{-1}$ |
| $\log K_f$ | — | $56{\cdot}872$ kcal. mole$^{-1}$ |

and equations giving free energy of formation from 432° to 1500°K. have been derived as follows[45, 210]:

$$P_4(l)+10Cl_2(g) \rightleftharpoons 4PCl_5(g); \quad \Delta G = -35{,}340+3{\cdot}44\,T\log T+12{\cdot}47T \text{ g.-cal. mole}^{-1}$$
$$P_4(g)+10Cl_2(g) \rightleftharpoons 4PCl_5(g); \quad \Delta G = -36{,}900+2{\cdot}01T\log T+19{\cdot}17T \text{ g.-cal. mole}^{-1}$$
$$P_2(g)+5Cl_2(g) \rightleftharpoons 2PCl_5(g); \quad \Delta G = -40{,}150+2{\cdot}01T\log T+21{\cdot}21T \text{ g.-cal. mole}^{-1}$$

The estimated error is ±3–5 kcal. mole$^{-1}$.

For the dissociation to phosphorus trichloride and chlorine in the gas phase, values of $\Delta H_0^\circ = -21{\cdot}32 \pm 0{\cdot}03$[43] and $20{\cdot}52 \pm 0{\cdot}16$ kcal. mole$^{-1}$ [185] were obtained using the available spectrographic data for $PCl_5$, $PCl_3$ and $Cl_2$. Free energy, heat content, and entropy changes, and equilibrium constant values for the dissociation reaction between 298° and 600°C. are summarized in Table V.[41]

*Table V.—$\Delta G^\circ$, $\Delta H^\circ$, $\Delta S^\circ$ and $K_{\text{atm.}}$ for the Reaction*
$PCl_5(g) = PCl_3(g)+Cl_2(g)$

| Temperature °K. | $\Delta G^\circ$ g.-cal. mole$^{-1}$ | $\Delta H^\circ$ g.-cal. mole$^{-1}$ | $\Delta S^\circ$ e.u. | $K_p$ atm. |
|---|---|---|---|---|
| 298·1 | 9140 | 22,130 | 43·6 | $2{\cdot}0 \times 10^{-7}$ |
| 400 | 4600 | 21,980 | 43·4 | $3{\cdot}1 \times 10^{-3}$ |
| 450 | 2350 | 21,890 | 43·4 | $7{\cdot}22 \times 10^{-2}$ |
| 500 | 100 | 21,800 | 43·4 | 0·904 |
| 550 | −2190 | 21,720 | 43·5 | 7·42 |
| 600 | −4420 | 21,640 | 43·4 | 40·8 |

A correlation of selected dissociation data based on a $\log_{10} K_p$ against $1/T$ relationship has provided a reasonable estimate of the percentage dissociation at elevated temperatures and pressures, thus:

| ref. | range °K. | $\log_{10} K_p$(atm.) | mean $\Delta H$ kcal. mole$^{-1}$ |
|---|---|---|---|
| 45, 210 | 462–623 | $9{\cdot}36-4810/T$ | 22·01 |
| 208 | 420–500 | $6{\cdot}66+1{\cdot}75\log T-4376/T$ | 22·00 |
| 41 | 298–600 | $9{\cdot}70-4860/T$ | 22·23 |
| calc.* | 400–800 | $9{\cdot}48-4840/T$ | 22·14 |
| mean | 300–800 | $9{\cdot}50-4830/T$ | 22·10 |

* From available thermodynamic data.[40, 42, 212–3]

Where $\alpha$ is the fraction of the pentachloride dissociated, and $P$ is the total pressure in atmospheres

$$K_p = \frac{\alpha^2 P}{1-\alpha^2} \quad \text{and} \quad \alpha = \sqrt{\frac{K_p}{K_p+P}}$$

Using these relationships values of $\alpha$ expressed as a percentage given in Table VI were calculated.[211]

*Table VI.—Dissociation at Elevated Temperatures and Pressures for the Reaction* $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$

| Temperature °K. | $K_p$ atm. | % dissociation at total pressure in atm. | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 10 | 50 | 100 | 200 |
| 300 | $2\cdot5\times10^{-7}$ | 0·05 | 0·02 | 0·007 | 0·005 | 0·004 |
| 400 | $2\cdot7\times10^{-3}$ | 5·2 | 1·6 | 0·73 | 0·52 | 0·37 |
| 500 | 0·69 | 64 | 25 | 12 | 8 | 6 |
| 600 | 28·2 | 98 | 86 | 60 | 47 | 35 |
| 800 | $29\cdot0\times10^{2}$ | 100 | 99·8 | 99·2 | 98·3 | 96·7 |

Enthalpy, free energy and entropy functions for phosphorus(V) chloride vapour between 298·1° and 600°K. derived[43] from the available spectroscopic data have been published.[41, 212–3] Heat capacities over the temperature range 298·1° to 500°K. were expressed[36] by the equation $C_p^\circ = 4{\cdot}739+0{\cdot}107329T–0{\cdot}0001192T^2$. A selection of the more recent values for each thermodynamic property, derived[185] from fuller spectrographic data, is given in Table VII, while a later study has extended the range of calculated values from 50 to 2000°K.[511]

*Table VII.—Thermodynamic Properties of* $PCl_5(g)$ *Ideal Gas State*

| Temperature °K. | $-\frac{G^\circ-H^\circ}{T}$ g.-cal. mole$^{-1}$ deg.$^{-1}$ | $H^\circ-H^\circ_0$ g.-cal. mole$^{-1}$ | $S^\circ$ g.-cal. mole$^{-1}$ deg.$^{-1}$ | $C^\circ_p$ g.-cal. mole$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|---|
| 298·1 | 68·425 | 5,485 | 86·734 | 26·75 |
| 300 | 68·539 | 5,508 | 86·900 | 26·77 |
| 350 | 71·470 | 6,877 | 91·118 | 27·91 |
| 400 | 74·147 | 8,292 | 94·878 | 28·71 |
| 500 | 78·989 | 11,216 | 101·420 | 29·73 |
| 600 | 83·183 | 14,218 | 106·880 | 30·32 |
| 700 | 86·903 | 17,267 | 111·570 | 30·70 |
| 800 | 90·267 | 20,347 | 115·701 | 30·95 |
| 900 | 93·294 | 23,450 | 119·349 | 31·13 |
| 1000 | 96·070 | 26,567 | 122·637 | 31·25 |
| 1200 | 101·064 | 32,830 | 128·422 | 31·42 |
| 1500 | 107·182 | 42,270 | 135·362 | 31·56 |

## Chemical Properties

Reduction of phosphorus(V) chloride in ether solution with excess of lithium, lithium boron or lithium aluminium hydrides leads only to phosphine, hydrogen and a solid hydride $PH_x$. It was concluded therefore[214] that phosphorus pentahydride does not exist.

In liquid ammonia solution, the phosphorus pentamide $P(NH_2)_5$ first formed dissociates irreversibly at 0°C. to give a mixture of tri- and tetrameric phosphonitrilic diamides $[PN(NH_2)_2]_n$. These, on further heating, lose ammonia according to the scheme:

$$[PN(NH_2)_2]_n \xrightarrow[\text{50–400°C.}]{} (PN.NH)_3 \xrightarrow[\text{480°C.}]{} P_3N_5 \xrightarrow[\text{700°C.}]{} P+N$$

i.e., with stepwise decomposition to phospham, phosphoric nitride and finally to elemental phosphorus and nitrogen.[215–8] Phosphorus(V) chloride in chloroform solution reacts vigorously with liquid ammonia at $-50$°C. to give a 36% yield of the solid trimer, $[PN(NH_2)_2]_3$.[219] With ammonium chloride in refluxing tetrachloroethane, phosphonitrilic chlorides, mainly the cyclic trimer and tetramer, are formed.[220–3] A similar reaction with ammonium bromide leads to the formation of some of the monobromo compound $P_3N_3Cl_5Br$,[224] but with ammonium or potassium fluoride the product is hexafluorophosphate according to the reaction,

$$PCl_5 + 6MF = MPF_6 + 5MCl^{225}$$

For a fuller account of these and related reactions, see Section XVIII.

Phosphorus pentachloride reacts with a midosulphonic acid in carbon tetrachloride solution to give trichlorophosphazosulphuryl chloride, m.p. 35° to 36°C.[226] (cf. Mellor, VIII, 1014) according to the equation:

$$2PCl_5 + H_2NSO_2H = POCl_3 + 3HCl + Cl_3P{=}NSO_2Cl$$

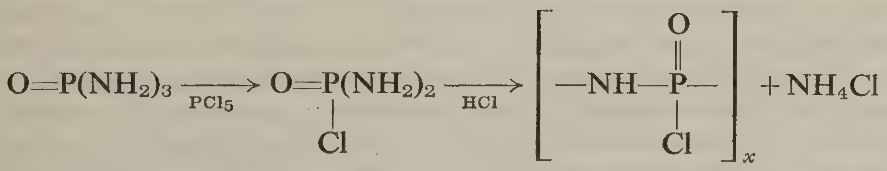
With sulphuryl diamide in a slow stream of dry air, the reaction

$$2PCl_5 + (H_2N)_2SO_2 = 4HCl + (Cl_3P{=}N)_2SO_2$$

occurring spontaneously at room temperature, is virtually complete in the presence of a slight excess of phosphorus(V) chloride (removable *in vacuo*) after keeping at 60° to 90°C. for 1 hr.[227] The product, m.p. 39·7° to 41°C., decomposes on distillation at 0·5 mm., is hygroscopic and reacts vigorously with water, ammonia, amines, alcohols and phenols. Recently,[228] reactions of similar type have been reported for the amidophosphoric acids and for triamidomonothiophosphate. Thus, with monoamidophosphoric acid in tetrachloroethylene solution (subject to removal of hydrogen chloride as it is formed) the reaction:

$$3PCl_5 + H_2N\text{–}PO(OH)_2 = 2POCl_3 + 4HCl + Cl_3P{=}NPOCl_2$$

proceeds vigorously and quantitatively at ordinary temperatures. The product, trichlorophosphazophosphoryl chloride, forms as colourless crystals, m.p. 35°C., which hydrolyze in water giving monoamidophosphoric, orthophosphoric and hydrochloric acids in dilute solution, ammonium phosphate in concentrated solution, or tetrasodium imidodiphosphate, $(NaO)_2PO\text{–}NH\text{–}PO(ONa)_2$, in excess of dilute caustic soda. With phosphorus(V) chloride and triamidophosphoric acid several reactions are possible. Thus, in the presence of hydrogen chloride, substitution of chlorine for an amino group occurs, and subsequent condensation leads to up to 80% yields of solid polymer according to:



$$O{=}P(NH_2)_3 \xrightarrow[PCl_5]{} O{=}\underset{\displaystyle Cl}{\underset{|}{P}}(NH_2)_2 \xrightarrow[HCl]{} \left[\text{—}NH\text{—}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle Cl}{\underset{|}{P}}}}\text{—}\right]_x + NH_4Cl$$

Removal of the hydrogen chloride as soon as it is liberated ensures formation of trichlorophosphazophosphoryl chloride in up to 50% yield as follows:

$$O{=}P(NH_2)_3 \xrightarrow[+2PCl_5]{} Cl_3P{=}NPOCl_2 + NH_4Cl + 2HCl + (NPCl_2)_x$$

Some phosphoryl chloride from the reaction

$$O{=}P(NH_2)_3 \xrightarrow[+PCl_5]{} POCl_3 + (NPCl_2)_2 + 2NH_3$$

as well as products from the reaction between phosphonitrilic chloride and phosphorus(V) chloride, of the type $(NPCl_2)_x,PCl_5$,[229] are also formed. With diamidophosphoric acid *ca.* 50% conversion to the trichlorophosphazophosphoryl chloride can be achieved, while with triamidothiophosphate, $SP(NH_2)_3$, in tetrachloromethane, the sulphur is readily replaced by 2 chlorine atoms and colourless crystals of tris-(trichlorophosphazo)-phosphorus dichloride separate. The low solubility of the latter compound in benzene, carbon tetrachloride, etc., and its high decomposition temperature, 170°C., and m.p., 200° to 202°C. (rapid measurement), point to an ionic formulation: $[Cl{-}P(N{=}PCl_3)_3]^+Cl^-$ rather than the covalent $Cl_2P(N{=}PCl_3)_3$. Cryoscopy in nitrobenzene, however, indicated[228] a molecular weight of 547; theory, 556.

The course of the reaction of phosphorus(V) chloride with amides of the general structure $RSO_2NHPOCl_2$ depends upon the nature of the group R.[512] The normal reaction is that given by the equation (1):

$$(1) \qquad RSO_2NHPOCl_2 + PCl_5 \rightarrow HCl + POCl_3 + RSO({=}NPOCl_2)Cl$$

while if R is very electronegative, trichlorophosphazosulphonyl derivatives are formed:

$$(2) \qquad RSO_2NHPOCl_2 + PCl_5 \rightarrow RSO_2N{=}PCl_3 + HCl + POCl_3$$

However, where R = $PhCH_2$ the reaction takes yet a third course:

$$\begin{aligned}(3) \quad & PhCH_2SO_2NHPOCl_2 + 2PCl_5 \\ & \qquad \rightarrow PhCH_2Cl + Cl_2S{=}NPOCl_2 + 2POCl_2 + HCl\end{aligned}$$

The products of reactions (1) and (3) can react further with more $PCl_5$, e.g.:

$$\begin{aligned}& CH_3SO({=}NPOCl_2)Cl + PCl_5 \rightarrow CH_3Cl + POCl_3 + Cl_2S{=}NPOCl_2 \\ & Cl_2S{=}NPOCl_2 + 3PCl_5 \rightarrow Cl_2 + SCl_2 + Cl_3P{=}NPOCl_2 \\ & Cl_3P{=}NPOCl_2 + 2PCl_5 \rightarrow POCl_3 + Cl_3P{=}NPCl_4{,}PCl_5\end{aligned}$$

By causing phosphorus(V) chloride to react with hydroxylamine hydrochloride in tetrachloroethane as solvent at 100°C. (hydrogen chloride and chlorine evolved) and subsequently removing the solvent and the concomitant product, phosphoryl chloride, at 45° to 60°C. *in vacuo*, a compound of composition $PCl_5NO$ was obtained,[230] b.p. 270° to 280°C. (decomp.), f.p. 34·1°C., $d_4^{38}$ 1·796 and $n_D^{38}$ 1·5260.

The graph of molar conductivity plotted against concentration for solutions of phosphorus(V) chloride in bromine passes first through a minimum and then through a maximum[231]; some initial ionization of the pentachloride and then of a chloride–bromide complex was suggested. Red-brown crystals of composition $PCl_5{,}5Br_2$, m.p. 25°C. (decomp.) were obtained[232] from carbon disulphide solutions of phosphorus(V) chloride–bromine mixtures on cooling. With iodine bromide–phosphorus(V) chloride mixtures in carbon tetrachloride solution, yellow crystals of composition $[PCl_4][ClIBr]$ were obtained.[233] The fusion diagram for the phosphorus(V) chloride–iodine chloride system shows a eutectic at 9·2 mole % $PCl_5$ (9·6°C.) and evidence of a maximum at 50 mole % $PCl_5$ (> 180°C., not realized due to excessive sublimation of the compound $PCl_6I$) analogous to that at 50 mole % $PBr_5$ (114·6°C.) in the phosphorus(V) bromide–iodine bromide system. Both equimolar complexes give electrically good conducting solutions in bromine, iodine chloride, methyl cyanide and nitrobenzene; their apparent molecular weights in the last solvent are approximately half of the expected values. The experimental results[234] may be summarized thus:

| Specific conductance (mho cm.$^{-1}$) of 5–15% solutions in: | $PCl_6I$ | $PBr_6I$ |
|---|---|---|
| Br at 25°C. | $2{\cdot}0 \times 10^{-2}$ | $2{\cdot}4 \times 10^{-2}$ |
| ICl at 45°C. | $2{\cdot}5 \times 10^{-2}$ | (in IBr) $3{\cdot}4 \times 10^{-2}$ |
| ICl at 55°C. | $3{\cdot}3 \times 10^{-2}$ | ( ,, ) $3{\cdot}8 \times 10^{-2}$ |
| $CH_3CN$ at 25°C. | $7{\cdot}7 \times 10^{-3}$ | $3{\cdot}4 \times 10^{-3}$ |
| $C_6H_5NO_2$ at 25°C. | $1{\cdot}3 \times 10^{-3}$ | $1{\cdot}1 \times 10^{-3}$ |
| Apparent mol. wt. in $C_6H_5NO_2$ solution | 185 | 355 |
| formula wt. | 370·7 | 637·5 |

The values indicate extensive dissociation according to the general equation: $PX_6I = [PX_4]^+ + [IX_2]^-$. An *X*-ray study of the $PCl_6I$ complex confirms[235–6] an ionic structure with tetrahedral $[PCl_4]^+$ and linear $[ClICl]^-$ ions.

The products of reaction between phosphorus(V) chloride and phosphorus(III) or (V) bromides with or without additional bromine have been studied by a number of investigators (see phosphorus chlorobromides pages 486–7); the system, however, is complex and remains incompletely clarified.

Phosphorus(V) chloride reacts with fluorosulphonic acid at −16°C. to give phosphoryl fluoride, hydrogen chloride, pyrosulphuryl chloride and chlorosulphonic acid,[237] cf.:

$$2SO_2(OH)Cl + PCl_5 \rightarrow S_2O_5Cl_2 + 2HCl + POCl_3 \quad \text{(Mellor, VIII, 1013)}$$

With dihydroxydifluoroboric acid, reactions are reported[238] as follows:

$$3H_3BO_2F_2 + 3PCl_5 \xrightarrow[\text{temperature}]{\text{at room}} BPO_4 + 2POCl_3 + 2BF_3 + 9HCl$$

$$3H_3BO_2F_2 + 3PBr_5 \xrightarrow[\text{on heating}]{} BPO_4 + 2POBr_3 + 2BF_3 + 9HBr$$

The chlorination rates for tantalum, niobium, titanium and zirconium oxides with liquid phosphorus(V) chloride, at 225°C. in sealed tubes, were found[239] to be dependent upon the method of preparation, the structural form and the specific surface area of the oxides.

COMPLEX FORMATION

Phosphorus(V) chloride gives rise to a large number of ionic complexes, evidence for which comes mainly from conductimetry in anhydrous solvent systems. Thus, in sulphuryl chloride solution it behaves as a chloride ion donor or 'solvo-base', and breaks in the conductimetric titration curves with solvo-acids coincide with[240] complex formation as follows:

| | | |
|---|---|---|
| — | $[PCl_4]_2.SbCl_7$ | $[PCl_4].SbCl_6$ |
| — | $[PCl_4]_2.TiCl_6$ | $[PCl_4].TiCl_5$ |
| $[PCl_4]_3.AsCl_6$ | $[PCl_4]_2.AsCl_5$ | $[PCl_4].AsCl_4$ |
| $[PCl_4]_4.SnCl_8$ | $[PCl_4]_2.SnCl_6$ | — |
| $[PCl_4]_3.SbCl_6$ | $[PCl_4]_2.SbCl_5$ | $[PCl_4].SbCl_4$ |

The existence of the compounds $[PCl_4]^+[AlCl_4]^-$ and $[PCl_4]^+[FeCl_4]^-$ was established by thermal analysis of the respective binary systems, as well as by cryoscopic, conductimetric and ionic transference methods in nitrobenzene[208, 241–2]; specific conductances at 25°C. for 0·13 to 0·77 M. solutions are of the order $10^{-2}$ mho cm.$^{-1}$ [241] The compounds (m.p. 343° and 332°C., respectively) are conveniently prepared from their components in chloroform or carbon tetrachloride solution. The former is insoluble in benzene, while the latter gives non-conducting solutions for which the freezing point depression corresponds to a molecular weight close to $FePCl_8$. Mixtures of phosphorus(V) chloride and stannic chloride in nitrobenzene show maximum conductivity ($4 \times 10^{-4}$ mho cm.$^{-1}$) at mole ratio 2:1; while for such solutions, cryoscopy indicates appreciable dissociation of the 2:1 complex according to: $[PCl_4]_2.SnCl_6 \rightleftharpoons 2[PCl_4]^+ + [SnCl_6]^{2-}$.[243] In phosphoryl chloride solutions of tin, titanium or zirconium tetrachlorides, antimony pentachloride, etc., addition of phosphorus(V) chloride causes a rapid increase in conductivity due to breakdown of the solvent complex (probably oxygen co-ordinated, see pages 497–502) and release of the complex-forming chloride.[244] With stannic chloride a subsequent drop in conductivity is accompanied by precipitation of the 2:1 complex, $[PCl_4]_2SnCl_6$; with zirconium chloride the conductivity titration curve shows breaks at the mole ratios $PCl_5:ZrCl_4 = 2:1$, 1:1 and 1:2.[245] The 1:2 complexes with zirconium or hafnium tetrachlorides are formed from stoicheiometric mixtures at 300°C., and repeated fractionation affords a separation of the zirconium (b.p. = 416°C.) from the hafnium compound, the latter concentrating in the tail fractions.[246-7] Similarly the complex $[PCl_4]_2TiCl_6$ can be prepared by boiling solid phosphorus(V) chloride with excess of titanium(IV) chloride for 1 hour. It is a yellow solid, slightly soluble in methylene chloride, and very soluble in nitromethane.[513] Titration of vanadium(IV) chloride with phosphorus(V) chloride in phosphoryl, arsenic(III) or thionyl chloride solution indicates formation of 2:1 and 3:1 complexes believed to contain $VCl_6^{--}$ and $VCl_7^{---}$ ions.[248] Two general preparative methods, viz., causing the metallic chloride to react either in hot phosphoryl chloride solution with phosphorus(V) chloride, or in thionyl chloride solution with phosphorus(III) chloride ($PCl_5$ is first formed) gave phosphorus(V) complexes[249] with each of the following:

Zn and Hg dichlorides
Al, Bi, Cr, Fe, Tl, B, Au trichlorides
Sn, Ti, Zr, Se, Te, Pt, V tetrachlorides
Sb, Mo, W pentachlorides

Reaction of phosphorus(V) chloride with metallic oxides generally leads to the formation of phosphoryl chloride. However, with chromium trioxide in phosphoryl, acetyl, or benzoyl chloride solutions, an orange-red precipitate of composition $CrPCl_7O_2$ is obtained. The same precipitate is formed by addition of phosphorus(V) chloride to chromyl chloride, both in solution in phosphoryl chloride; the formula $PCl_4^+.CrO_2Cl_2^-$ was proposed for the product,[250] wherein the negative part may be polymeric. The uranium complex $UCl_5,PCl_5$ forms as orange-red crystals on mixing anhydrous uranium trioxide (orange, reactive form) with phosphorus(V) chloride and recrystallizing from phosphoryl chloride. In this solvent it behaves as $PCl_4^+.UCl_6^-$.[251] With nitrosyl perchlorate in phosphoryl or arsenic(III) chloride solution, phosphorus(V) chloride decomposes to phosphorus pentoxide and phosphoryl chloride; nitrosyl chloride, chlorine dioxide and chlorine are also formed.[250]

Conductimetric titration of tellurium(IV) chloride in arsenic(III) chloride solution with phosphorus pentachloride showed breaks at mole ratios $PCl_5:TeCl_4 = 2$, 1 and 0·5[252]; the respective compounds can be isolated by evaporation of the solvent. Cryoscopic and conductimetric data for 0·1 M. solutions of phosphorus(V) chloride in arsenic(III) chloride indicate that the equilibrium:

$$2AsCl_3 + PCl_4^+ + PCl_6^- \rightleftharpoons 2PCl_4^+ + 2AsCl_4^-$$

lies 70% to the left. Evaporation of more concentrated solutions gave hygroscopic prismatic crystals of composition $2PCl_5,5AsCl_3$, m.p. 40°C. Addition of phosphorus(V) chloride to antimony(III) chloride in chloroform solution precipitates white hygroscopic crystals of composition $2PCl_5,4SbCl_3$, m.p. 106°C. (decomp.). Cryoscopic and conductimetric evidence for the latter compound in antimony(III) chloride solution favours its formulation as the solvate $[PCl_4]^+[PCl_6]^-,4SbCl_3$ rather than as the ion donor compound $[PCl_4]^+[SbCl_4]^-,SbCl_3$. Specific conductances for 0·05 M. solutions of $P_2Cl_{10}$, $P_2Cl_{10},5AsCl_3$ and $P_2Cl_{10},4SbCl_3$ in acetonitrile at 20°C. were 1·4, 2·1 and $3{\cdot}0 \times 10^{-3}$ mho cm.$^{-1}$, respectively.[253]

Titration of phosphorus(V) chloride or of tetrachlorophosphonium fluoride with tetraethylammonium chloride in the same solvent[198] provided no evidence of any reaction such as: $PCl_4^+ + 2Cl^- \rightarrow PCl_6^-$. The formation of $PCl_6^-$ ions in the acetonitrile–hydrogen chloride–phosphorus(V) chloride system, however, was confirmed from conductivity and ion transfer evidence[254]; the formula $[(MeCN)_xH]^+[PCl_6]^-$ was proposed for the complex. Conductimetric titrations, in iodine chloride solution, with antimony(V) chloride[255] show phosphorus(V) chloride to be typically solvobasic, but against potassium, cæsium or tetramethylammonium chlorides it is solvo-acidic.[256-7] From the latter group of titration solutions in iodine chloride, or from those from precisely similar titrations in arsenic(III) chloride or phosphoryl chloride solution, no compounds of type $MPCl_6$ could be isolated. However, from phosphorus(V) chloride in arsenic(III) chloride solution saturated with chlorine, the compound $AsPCl_{10}$ was obtained[258]; it is unstable, insoluble in carbon tetrachloride and thought to contain $AsCl_4^+$. The amphoteric property of phosphorus(V) chloride in both thionyl and phosphoryl chloride solutions has also been demonstrated.[259] In thionyl chloride, titrations with tetramethylammonium chloride (solvo-basic) and with antimony(V) chloride (solvo-acidic) were followed conductimetrically, potentiometrically and by the use of acid–base indicators.[260–1] In phosphoryl chloride solution against tetraethylammonium chloride, white finely crystalline tetraethylammonium hexachlorophosphonate, $Et_4NPCl_6$, was precipitated.[262] Phosphorus(V) chloride is readily soluble in liquid hydrogen chloride and behaves in such solutions as a strong solvo-base thus:

$$PCl_4.PCl_6 + 2HCl \rightarrow 2PCl_4^+ + 2HCl_2^-$$

The molar conductance at 0·2 M. concentration is 25 mho cm.$^2$ mole$^{-1}$. Conductimetric titration with boron trifluoride shows a break at mole ratio 1:1; the solid complex corresponding to this break, and for which infra-red spectroscopy confirmed the ionic formula $[PCl_4]^+[BF_3Cl]^-$, was separated on evaporation of the solvent.[263–5] Titration in the same medium with boron trichloride gave a white precipitate of composition $PCl_5,2BCl_3$, which decomposed to the 1:1 complex and boron trichloride at room temperature.[263–5] A white 1:1 $BCl_3,PCl_5$ complex is precipitated by passing boron trichloride into refluxing phosphorus(V) chloride in triethylamine solution. This compound melts with decomposition; at 300°C. in a sealed tube the products are chlorine and a boron phosphide of composition varying between BP and $B_5P_3$.[266–7, 514] A general review of the addition compounds of the Group V pentahalides has appeared.[515]

1:1 Adducts were reported[268] between phosphorus(III) or (V) chlorides and triethylamine; the results, however, were not confirmed in a later study using purified reagents in an all-glass high vacuum apparatus. Under such conditions[162–3] with trimethylamine, triethylamine or trimethylarsine, reduction of phosphorus(V) to phosphorus(III) chloride occurs:

$$\left.\begin{array}{l} Me_3N \xrightarrow[+PCl_5 \text{ at } 100°C.]{} \underset{\text{white}}{(Me_3N)_2Cl_2} + PCl_3 \\ Et_3N \xrightarrow[+PCl_5 \text{ at } 20°C.]{} \underset{\text{orange}}{Et_3NCl_2} + PCl_3 \end{array}\right\} \text{cf. } Me_3N \xrightarrow[+SbCl_5]{} 1:1 \text{ complex}$$

$$Me_3As \xrightarrow[+PCl_5 \text{ at } 20°C.]{} Me_3AsCl_2 + PCl_3$$

$$\text{cf.} \left\{\begin{array}{l} Et_3N + PCl_3 \xrightarrow[-78° \text{ to } 0°C.]{} \text{no reaction} \\ Me_3N + PCl_3 \xrightarrow[-78° \text{ to } 0°C.]{} 1:1 \text{ complex*} \\ Me_3As + PCl_3 \xrightarrow[-29.5°C.]{} 1:1 \text{ complex*} \end{array}\right.$$

* see page 475.

With trimethylstibine some elemental phosphorus is formed:

$$Me_3Sb \xrightarrow[+PCl_5 \text{ (or } PCl_3\text{) at } 0°C.]{} Me_3SbCl_2 + P$$

Trimethylphosphine forms a 2:1 complex with both phosphorus(V) and (III) chlorides; (cf. it forms both a 2:1 and a 1:1 complex with antimony(V) chloride)

$$Me_3P \xrightarrow[+PCl_5 \text{ in bromobenzene at } 0°C.]{} (Me_3P)_2,PCl_5$$

$$Me_3P \xrightarrow[+PCl_3 \text{ at } 0°C.]{} (Me_3P)_2,PCl_3$$

Phosphorus(V) chloride is insoluble in boron trichloride at 0°C. but reacts in the vapour state or in carbon tetrachloride solution to give a 1:1 complex, $PCl_5,BCl_3$.

The complex is also formed by chlorination of phosphorus(III) chloride–boron trichloride mixtures at −78°C. (see page 475). It sublimes with reversible dissociation at 340°C. in a sealed tube[269]:

$$PCl_5,BCl_3 \rightleftharpoons PCl_3 + Cl_2 + BCl_3$$

Phosphorus(V) chloride with gallium chloride in carbon tetrachloride gives a 1:1 complex, and the respective high melting points, viz.:

| | | |
|---|---|---|
| | $PCl_5,GaCl_3$ | m.p. 368° to 371°C.[269] |
| | $PCl_5,BCl_3$ | sublimes at 340°C.[269] |
| cf. | $PCl_5,AlCl_3$ | m.p. 375° to 379°C.[208] |

compared with those of their components, indicate probable salt-like structures for each of these compounds.

## PHOSPHORUS CHLOROBROMIDES

Interaction between phosphorus(III) and (V) chlorides and bromides, bromine and chlorine leads to various crystalline and liquid phases of mixed composition, the nature of the compounds formed having received much attention in the past thirty years but without, as yet, it being completely clarified.

Early workers[270–2] obtained liquid phosphorus(III) and crystalline phosphorus(V) chlorobromides either by substitution of elemental bromine into phosphorus(III) or (V) chlorides, or by reaction between the respective phosphorus(III) and (V) halides. No compound of composition $PCl_3Br_2$ was so isolated,[270–1] but two series of unstable polybromides, viz: $PCl_2Br_n$ (with $n > 3$) and $PCl_3Br_n$ (with $n = 4$ to 18) thought to be derived from $PCl_2Br$ + bromine and from $PCl_4Br + PCl_2Br$ + bromine, respectively, were postulated.[272] Equilibration of phosphorus(V) chloride/bromide mixtures at 135°C. in sealed tubes gave coloured crystalline and liquid phases of varied composition.[273–4] The same reaction mixtures in carbon disulphide solution gave similar products.[275] With chlorine and phosphorus(III) bromide or with bromine and phosphorus(III) chloride, yellow crystals of limiting compositions $PClBr_4$ or $PCl_4Br$ were obtained. Crystalline $PCl_4Br$ loses chlorine at 135°C. to give crystalline $PCl_{4\cdot5}Br_{0\cdot5}$ and mixed liquid phases.[276] Recrystallization of $PCl_4Br$ from carbon disulphide produced only crystals of higher chlorine content, while from products of composition close to $PClBr_4$ and $PCl_{0\cdot5}Br_{4\cdot5}$ crystals of lower chlorine content than the original were always obtained.[275] Evidence that three of the chlorine atoms in $PCl_4Br$ are attached to the phosphorus in a manner different from the fourth and from the bromine atom was claimed[277] from the manner of the reaction with phenol, PhOH; in this reaction the hydrogen bromide is released only after a subsequent hydrolysis step:

$$PCl_4Br + 3PhOH \rightarrow (PhO)_3PClBr + 3HCl$$
$$(PhO)_3PClBr + H_2O \rightarrow (PhO)_3PO + HBr + HCl$$

Maxima in the fusion diagram for the phosphorus(III) chloride–bromine system occur at 24·5° and 37°C. corresponding to the compositions $PCl_3Br_{18}$ and $PCl_3Br_4$, respectively. A maximum in the viscosity curve occurs at $PCl_3Br_8$ and in both the density and the electrical conductance curves at $PCl_3Br_{18}$. The conductances of the various complexes in nitrobenzene solution increase in the order $PCl_3Br_4 < PCl_3Br_8 < PCl_3Br_{18}$ and results from ionic migration experiments have suggested the general structure $[PCl_3Br]^+[Br(Br_2)_n]^-$. Orange red crystals of composition $PCl_3Br_4$, m.p. 36·7°C., separated on cooling from heated phosphorus(V) chloride/bromide or from phosphorus(III) bromide/phosphorus(V) chloride mixtures of mole ratio 3:2. With excess of phosphorus(III) bromide the second mixture gives yellow crystals of composition $PClBr_4$.[278–80]

A spectrophotometric study provided no evidence of compound formation between phosphorus(III) chloride and bromine in carbon tetrachloride or nitrobenzene solution,[281] but a cryoscopic study in the latter solvent[282] has shown the existence of equilibria involving both $PX_5$ and $PX_7$ species. From such solutions in carbon tetrachloride, substances approximating to $PCl_3Br_7,CCl_4$ and $PCl_3Br_7,2CCl_4$ were crystallized; these, however, decomposed with loss of bromine on attempting to remove the carbon tetrachloride.[282] Direct reaction between phosphorus(III) chloride and bromine led[281] to the formation of an unstable crystalline aggregate (composition $PCl_3Br_{5\cdot7}$, m.p. 36·8° to 38°C.) which, after keeping under vacuum at 30°C. and further heating at 50°C., yielded a stable yellow sublimate ofcomposition $PCl_{4\cdot67}Br_{0\cdot33}$, m.p. 145° to 148°C., refractive index 1·64, and shown by *X*-ray diffractometry to be a single compound with unit cell equal to $P_{12}Cl_{56}Br_4$.[281]

Dropwise addition of bromine to phosphorus(III) chloride in arsenic(III) chloride solution, and subsequent cooling to 0°C., gave[283] crystals of tetrachlorophosphonium pentachlorobromophosphate, $[PCl_4]^+[PCl_5Br]^-$, separable by filtration and evacuation at 0°C. The crystals were strongly hygroscopic, reacted vigorously with water liberating bromine, had a typically crystalline *X*-ray powder diagram, and decomposed at 142°C. (sealed tube) or on dissolution in non-polar solvents to phosphorus(V) chloride and phosphorus(V) bromide. Fluorination takes place in arsenic(III) chloride solution according to:

$$3[PCl_4][PCl_5Br] + 6AsF_3 \rightarrow 3[PCl_4][PF_6] + 5AsCl_3 + AsBr_3$$

The molar conductance for 0·048 and 0·2 M. solutions of the product in acetonitrile at 17°C. was 8·16 and 11·0 mho cm.$^2$ mole$^{-1}$ respectively. The compound is thought[283] to be the limiting case for the series of others with variable compositions described by earlier authors.

## PHOSPHORYL CHLORIDE, $POCl_3$

### Preparation

Phosphoryl chloride can be obtained by the action of phosgene upon molten ferric phosphate, metaphosphoric acid or heated calcium phosphate,[284–8] of chlorine upon heated mixtures of carbon with either phosphate rock,[14–5, 17, 289–97] alkaline earth metaphosphate,[298–9] aluminium phosphate[176, 300] or phosphoric acid,[18, 301–3] or alternatively upon phosphoric acid–water–phosphorus trichloride,[304] phosphorous acid–phosphorus in phosphoryl chloride[305] or phosphorus pentoxide–phosphorus trichloride[306–8] mixtures at reflux temperatures. The last process, formulated

$$P_2O_5 + 3PCl_3 + 3Cl_2 = 5POCl_3$$

is commonly used on the commercial scale and gives a 95 to 98% yield based on phosphorus pentoxide. Phosphoryl chloride is also manufactured by direct oxidation of phosphorus(III) chloride with gaseous oxygen.[27–9, 309–12] By admitting the oxygen as fine gas bubbles at 3 ft. depth, complete absorption occurs with up to 95 to 98% conversion at reflux temperatures. Traces of iron, copper and vulcanized rubber act as inhibitors while manganese oxides, phosphorus acids, etc., have been suggested as catalysts. Numerous other variations of the process occur in the patent literature.[313–6] The simultaneous reaction of chlorine and oxygen with yellow phosphorus gives good yields of phosphoryl chloride if the O:Cl ratio is 30% in excess of that required by the equation:

$$P + \tfrac{1}{2}O_2 + 1\tfrac{1}{2}Cl_2 \rightarrow POCl_3$$

Below this ratio phosphorus(V) chloride is formed, and above it, pyrophosphoryl chloride. The primary step in the reaction appears to be attack on the phosphorus by oxygen, since the reaction rates observed are much higher than would be expected if oxidation of phosphorus(III) chloride were a rate-determining step.[517] Liquid or gaseous sulphur dioxide–chlorine mixtures react with phosphorus in phosphorus oxychloride or with phosphorus(III) chloride[317–8] according to:

$$P + SO_2 + \tfrac{5}{2}Cl_2 = POCl_3 + SOCl_2$$
$$PCl_3 + SO_2 + Cl_2 = POCl_3 + SOCl_2$$

Sulphur trioxide with phosphorus(III) chloride gives phosphoryl chloride and sulphur dioxide.[117] Phosphoryl chloride is also formed by the interaction of phosphorus pentoxide and aluminium(III) chloride in an alkali halide melt.[518] Labelled phosphoryl chloride is conveniently obtained from phosphorus(V) chloride and $^{32}$P phosphoric acid,[319] or (for small amounts) by exchange with aqueous $^{32}$P phosphoric acid at 150°C.[320]

### Physical Properties

The boiling point of phosphoryl chloride is variously reported between 105·1° and 107·4°C.[27, 34, 41, 321–2] The value 107·4°C. is regarded[33] as the more reliable, and much of the variability in the literature is probably due to the presence of hydrochloric acid, phosphoric acid or phosphorus(III) chloride impurities which are difficult to eliminate. An apparatus for the preparation of pure phosphoryl chloride, permitting fractionation in an entirely inert atmosphere, was recently described.[324] The determined boiling point was 107·7 ± 0·1°C., and the specific conductance $2 \times 10^{-8}$ mho cm.$^{-1}$ The available vapour pressure data may be summarized:

| Range °C. | $\log_{10} p$(mm.) | Latent heat of vaporization (kcal. mole$^{-1}$) | B.p. °C. | Ref. |
|---|---|---|---|---|
| 75–107·4 | $7{\cdot}9816 - 1940{\cdot}7/T^{(a)}$ | 8·90 | 107·37 | 33 |
| 50–107·4 | $7{\cdot}734 - 1846/T^{(b)}$ | 8·41 | 107·4 | 33 |
| 41–113 | $7{\cdot}782 - 1864/T^{(c)}$ | 8·54 | 107·2 | 34 |
| 20–105 | $7{\cdot}7386 - 1836{\cdot}4/T$ | 8·39 | 105·3 | 325, 326 |
| 0–60 | $7{\cdot}7886 - 1850{\cdot}2/T$ | 8·45 | 104·0 | 35 |
| 7–25 | $8{\cdot}1395 - 1982{\cdot}9/T$ | 9·06 | — | 327 |
| | | 9·22$^{(d)}$ | — | 327 |

(a) From vapour pressure and boiling point measurements
(b) From vapour pressure data[325–6] plus boiling point measurements.
(c) From boiling point measurements.
(d) From calorimetric measurement at 25°C., $p = 30{\cdot}9$ mm.

Vapour–liquid equilibrium data[34] confirm that the $POCl_3$–$PCl_3$ system is reasonably ideal. The melting point of phosphoryl chloride is given as 1·18 ± 0·05°,[327] 1·20°[328] and 1·15 ± 0·05°C.[329] The latent heat of fusion is 3132 ± 3 g.-cal. mole$^{-1}$ [327] and the cryoscopic $K$ is given as 1°C. depression per 2·2 mole % impurity.[328] The heat capacity for the solid and liquid states between 13° and 304°K. has been measured[327] (data included in Table VIII) and for the vapour state between 298·1° and 1000°K. was expressed[36] by

$$C_p^\circ = 23{\cdot}294 + 0{\cdot}002185T - 353400/T^2 \text{ g.-cal. deg.}^{-1} \text{ mole}^{-1}$$

Remeasurement of the heat of hydrolysis for the reaction:

$$POCl_3(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$$

together with the available thermal data gave values of $\Delta H$ and $\Delta H^\circ_{f25}$ in kcal. mole$^{-1}$ as:

| Ref. | 37 | 38 | 330 | 519 |
|---|---|---|---|---|
| $\Delta H$ | −79·9 ± 3 | −80·4 | −79·6 ± 0·5 | −80·2 |
| $\Delta H^\circ_{f25}(l)$ | −144·4 | −143·8 | — | −143·4 |
| $\Delta H^\circ_{f25}(g)$ | — | −134·3 | — | — |

The O═PCl$_3$ bond dissociation energy calculated therefrom is 121·8 kcal. mole$^{-1}$,[38] cf. 119·3 (from hydrolysis data[38]) and 129·8 kcal. mole$^{-1}$ (from a direct measurement of the heat of oxidation of $PF_3$ gas[331]) for the dissociation energies of the P═O bonds in $POBr_3$ and $POF_3$, respectively. These values were taken[38] as indicating a considerable degree of double bond character in the O–PX$_3$ linkage. The above values for standard heat of formation supersede those given elsewhere.[40–2] The free energy ($\Delta G_f^\circ$) and equilibrium constant of formation (log $K_f$) for phosphoryl chloride vapour at 25°C. are given[40–2] as $-130·3$ kcal. mole$^{-1}$ and 95·508, respectively; enthalpy and free energy functions for the vapour in the temperature range 298·1° to 1000°K. have been evaluated[43] and are further tabulated[41] together with the corresponding entropy values. The entropy of the ideal gas at 1 atm. and 298·15°K. derived from calorimetric data is 77·75 g.-cal. mole$^{-1}$ deg.$^{-1}$ [327]; the calculated value from a selected assignment of the fundamental frequencies being 77·77 g.-cal. mole$^{-1}$ deg.$^{-1}$ The same authors[327] have calculated the thermodynamic properties for solid or liquid phosphoryl chloride in the temperature range 15° to 300°, and for the vapour state in the range 15° to 500°K.; a selection of these more recent values is made in Table VIII.

*Table VIII.—Thermodynamic Properties of Phosphoryl Chloride*

| Temperature °K. | $-\frac{G^\circ - H^\circ}{T}$ g.-cal. mole$^{-1}$ deg.$^{-1}$ | $H^\circ - H_0^\circ$ g.-cal. mole$^{-1}$ | $S^\circ$ g.-cal. mole$^{-1}$ deg.$^{-1}$ | $C_p^\circ$ g.-cal. mole$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|---|
| Solid and liquid | | | | |
| 15 | 0·220 | 9·6 | 0·857 | 2·308 |
| 50 | 3·310 | 261·6 | 8·541 | 10·466 |
| 80 | 6·374 | 629·8 | 14·246 | 13·909 |
| 120 | 10·088 | 1262·3 | 20·607 | 17·604 |
| 160 | 13·418 | 2028·5 | 26·096 | 20·653 |
| 200 | 16·452 | 2908 | 30·994 | 23·276 |
| 240 | 19·252 | 3887 | 35·449 | 25·627 |
| 273·15 | 21·429 | 4770 | 38·887 | 27·596 |
| 274·33 (s) | 21·504 | 4801 | 39·006 | 27·672 |
| 274·33 (l) | 21·504 | 7934 | 50·423 | 33·046 |
| 280 | 22·096 | 8121 | 51·099 | 33·001 |
| 298·15 | 23·926 | 8722 | 53·174 | 33·169 |
| Ideal gas at 1 atm. pressure | | | | |
| 15 | 35·512 | 119·2 | 43·461 | 7·949 |
| 50 | 45·100 | 402·5 | 53·150 | 8·548 |
| 100 | 50·952 | 911·3 | 60·065 | 11·960 |
| 150 | 54·927 | 1591 | 65·536 | 15·102 |
| 200 | 58·179 | 2410 | 70·218 | 17·430 |
| 250 | 61·003 | 3324 | 74·298 | 19·109 |
| 273·15 | 62·204 | 3774 | 76·018 | 19·723 |
| 274·33 | 62·264 | 3797 | 76·104 | 19·752 |
| 298·15 | 63·436 | 4274 | 77·770 | 20·298 |
| 300 | 63·525 | 4311 | 77·896 | 20·336 |
| 350 | 65·811 | 5352 | 81·103 | 21·262 |
| 400 | 67·907 | 6434 | 83·992 | 21·980 |
| 450 | 69·842 | 7547 | 86·614 | 22·549 |
| 500 | 71·641 | 8687 | 89·015 | 23·007 |

Fundamental frequency assignments were made[332–5] from the available infra-red and Raman data, and force constant values derived[334, 336–7] by E. B. Wilson's method are given in Table X, page 491. Other authors[332–3, 335] have attempted a more complete solution using the available data for $PX_3$. The same authors have re-calculated the thermodynamic properties for gaseous phosphoryl chloride between 50° and 1600°K. The calculated values[332–3, 335] are reasonably close to those given in Table VIII.

Ebullioscopy with 4 chloro-1:3-dinitrobenzene as solute gave $K$ (unit molal elevation) = 5·58°C.[338] (cf. 5·02 calculated from the latent heat of vaporization which is 8·39 kcal. mole$^{-1}$,[325–6] and 5·47[339] from the specific cohesion and b.p. 107·3°C.). The density, $d_4^t$, from 0° to 105°C. is given by:

$$d_4^t = 1{\cdot}7116 - 1{\cdot}839 . 10^{-3}t + 1{\cdot}66 . 10^{-7}t^2 - 5{\cdot}5 . 10^{-9}t^3$$ [340–1]

and subsequent density determinations noted in the literature serve only to confirm these early measurements. Density and viscosity data are briefly summarized in Table IX.

*Table IX.—Density and Viscosity Data for Phosphoryl Chloride*

| °C. | $d_4^t$ (g. c.c.$^{-1}$) | η (poise) | | | | |
|---|---|---|---|---|---|---|
| Ref. | 340, 341 | 342, 69(a) | 72(b) | | 343(c) | 323 |
| | | | | % deviation (obs. − calc.) | | |
| 0 | 1·7116 | — | 0·01445 | +1·1 | — | — |
| 5 | 1·7024 | 0·01384 | — | — | 0·01369 | 0·01368 |
| 15 | 1·6840 | 0·01209 | 0·01141 | −0·7 | 0·01203 | 0·01184 |
| 25 | 1·6657 | 0·01077 | 0·00999 | −0·7 | 0·01072 | 0·01018 |
| 35 | 1·6462 | 0·00979 | 0·00887 | −1·1 | 0·00965 | 0·00892 |
| 50 | 1·6194 | 0·00868 | 0·00737 | −0·9 | 0·00839 | 0·00750 |
| 60 | 1·6007 | 0·00803 | — | — | 0·00771 | 0·00687 |
| 65 | — | — | 0·00646 | +0·3 | — | — |
| 70 | 1·5818 | 0·00742 | — | — | 0·00727 | 0·00614 |
| 80 | 1·5628 | 0·00685 | 0·00554 | +1·3 | 0·00668 | 0·00564 |
| 95 | 1·5338 | — | — | — | 0·00607 | — |
| 105 | 1·5140 | — | — | — | — | — |
| b.p. | 107·23 | — | 105·9 (762 mm.) | | 105·8 | 107·4 |
| $d_4^{25}$ | 1·6657 | — | 1·6676 | | — | 1·6656 |
| $d_4^{20}$ | 1·6750 | — | — | | 1·6480 | — |

(a) Conform to the Bachinskii[70] formula with $C = 0{\cdot}00712$, $\omega = 0{\cdot}5352$.
(b) Calculated values from the Andrade[71] formula with $A = 0{\cdot}0005014$, $C = 506$.
(c) Interpolated from a log $\eta$ versus $1/T$ plot (range 4·5° to 105°C.).

Cryoscopy in benzene gave mol. wt. = 166, indicating an association factor of 1·08.[75] However, the constancy of the parachor data over the temperature range 15° to 65°C. thus:

| °C. | Surface tension[344] (dyne cm.$^{-1}$) | Parachor | |
|---|---|---|---|
| 15 | 32·77 | 217·1 | b.p. 108·7°C. at 769 mm. |
| 49 | 28·36 | 217·7 | $d_4^{25}$ = 1·671 |
| 65 | 26·75 | 218·1 | |

and the conformity of the viscosity/temperature relationship with the Andrade[71] exponential formula, indicate[344] that phosphoryl chloride is an essentially normal liquid. Further, the parachor values for the phosphoryl chloride–benzene and for the phosphorus(III) chloride–benzene systems were found[79] to be additive on a mole fraction basis. Molar polarization and dipole moment values for both phosphoryl and thiophosphoryl chlorides, and bond moments for the semipolar $P \rightarrow O$ and $P \rightarrow S$ bonds (see Table X) were obtained[345–6] from dielectric constant measurements of their solutions in benzene together with the available dipole moment data[50] for phosphorus(III) chloride.

The molar diamagnetic susceptibility ($-\chi_m \times 10^6$) was found to be 68·9,[63] 61·8[347] c.g.s. units. Ultrasonic measurements[84] lead to the values of molar sound velocity and adiabatic compressibility shown in Table III.

The ultra-violet absorption spectra (2400 to 1850 A.) for gaseous phosphoryl chloride and phosphorus trichloride have been published.[348] The former shows low

*Table X.—Molar Polarization* (c.c.), *Refractive Index, Dipole and Bond Moments* (*Debyes*) *for* $POCl_3$ *and* $PSCl_3$

| Compound | °C. | $P_M$ | $n_D$ | Molar refraction | Dipole moment | Bond moment P → O | Ref. |
|---|---|---|---|---|---|---|---|
| $POCl_3$ | 10 | 147·0 | — | — | 2·36 | — | 345 |
| | 25 | 143·4 | 1·4582 | 25·13 | 2·39 | 3·5 | 345 |
| | 40 | 140·0 | — | — | 2·41 | — | 345 |
| | 60 | 133·4 | — | — | 2·42 | — | 345 |
| | 20 | 147·5 | 1·4606 | 25·1 | 2·40 | 3·56 | 346 |
| | 20 | — | 1·4607 | — | — | — | 34 |
| | | — | — | — | — | 3·25 | 49 |
| | | | | | | P → S | |
| $PSCl_3$ | 25 | 74·3 | 1·5432 | 32·8 | 1·41 | 2·5 | 345 |
| | | — | — | — | — | 2·23 | 49 |
| $PSBr_3$ | | — | — | — | — | 2·00 | 49 |

absorption at 2100 A. and a broad maximum at 1960 to 1850 A., while the latter shows strong absorption below 2400 A. with a maximum at 2170 ± 5 A., followed by a minimum at 1960 A. and another increase in absorption which had not reached a maximum at the limits of the instrument at 1850 A.

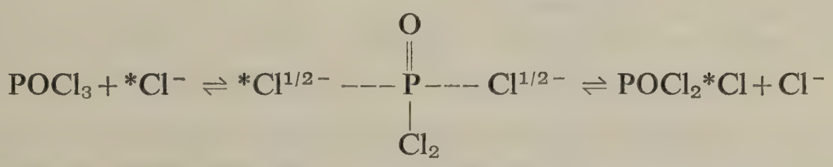
## Chemical Properties

### CHLORINE EXCHANGE

$^{35}Cl$ exchange in the vapour phase using labelled hydrogen chloride is much more rapid with phosphorus(III) chloride than with phosphoryl chloride.[88] Rapid exchange of chloride ion (complete within the time of separation at 20°C.) occurs in dilute solutions of $^{36}Cl$-labelled tetraethylammonium chloride in phosphoryl chloride[349–50]; conductimetry for such solutions showed the solute to be completely dissociated.[349] A kinetic study of the above reaction carried out in chloroform, nitrobenzene or methyl cyanide solvent indicated a bimolecular mechanism, the exchange being of first order with respect to chloride ion and to phosphoryl chloride. It was concluded[349] that the reaction in phosphoryl chloride medium proceeds either through direct formation of $[POCl_4]^-$ according to:

$$POCl_3 + {}^*Cl^- \rightleftharpoons [POCl_3][Cl^*]^- \rightleftharpoons POCl_2{}^*Cl + Cl^-$$

or through a substitution intermediate state[351] written as:



$$POCl_3 + {}^*Cl^- \rightleftharpoons {}^*Cl^{1/2-} --- \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Cl_2}{|}}{P}} --- Cl^{1/2-} \rightleftharpoons POCl_2{}^*Cl + Cl^-$$

rather than through self-ionization of the solvent. Exchange between $^{36}Cl$-labelled liquid nitrosyl chloride and phosphoryl chloride solute is slow[352] and is assumed to occur *via* the formation of chloride ions; the concentration of such ions in the solvent was calculated to be $10^{-8}$ g. ion/litre.

### REORGANIZATION IN THE PHOSPHORYL HALIDES

Phosphoryl chloride/bromide or thiophosphoryl chloride/bromide mixtures undergo ligand exchange to form mixed chlorobromides when kept in sealed tubes at elevated temperatures. Quantitative nuclear magnetic resonance methods applied to such mixtures *in situ* have shown[91] that equilibrium is attained at 130°C. within seven days; the compositions then approximate to those predicted for completely randomized ligand exchanges. Such mixtures, originally of 2:1 molar ratios of chloride to bromide, reached equilibrium in a few hours at 200°C. and contained 42 to 46% of mixed phosphoryl or thiophosphoryl halides respectively, isolated by fractionation under reduced pressure. For the mixed systems $POCl_3$–$PBr_3$ and $POBr_3$–$PCl_3$, n.m.r. analysis after 4 weeks at 110° or 1 week at 200°C. shows the presence of all eight possible compounds, viz.: $POCl_3$, $POCl_2Br$, $POClBr_2$, $POBr_3$, $PCl_3$, $PCl_2Br$, $PClBr_2$ and $PBr_3$.[92] Completely randomized interaction is expressed by two equations of each type:

$$\begin{aligned} 2PX_2Y &= PX_3+PXY_2 \\ 2POX_2Y &= POX_3+POXY_2 \end{aligned}$$

for which $K_1=K_2=K_3=K_4=0{\cdot}33$, and one equation of mixed type, for which the general expression:

$$PX_iY_{3-i}+POX_jY_{3-j} \rightleftharpoons PX_nY_{3-n}+POX_{i+j-n}Y_{3-(i+j-n)}$$

gives $K_5=1$. The experimental values for $K_{1-4}$ range from 0·3 to 0·6, with a single value of $K_5=5$. However, numerical significance cannot be attached to the last figure, since the equation used is but one of fourteen possible expressions having widely differing values for departures of $K_{1-4}$ from 0·33.[92]

### HYDROLYSIS OF PHOSPHORYL CHLORIDE

Titrations with standard baryta[353] afforded early evidence that the hydrolysis in ice-water proceeds through dichlorophosphoric acid. Thus neutralization to the thymolphthalein end point required two equivalents initially and, on standing, further increments up to a total of six equivalents, in accordance with:

$$POCl_3 \xrightarrow[+H_2O]{} H[PO_2Cl_2]+HCl \xrightarrow[+2H_2O]{} H_3PO_4+3HCl$$

The latter stage is accompanied by precipitation of all the phosphorus as barium orthophosphate, $Ba_3(PO_4)_2$. Addition of an equimolar quantity of water to phosphoryl chloride at −75°C., followed by melting and careful reaction at −25° to −10°C., gave pure dichlorophosphoric acid,[98] confirmed by analysis of its insoluble nitron and brucine salts. With 2 moles of water to 1 of phosphoryl chloride at temperatures up to 10°C., dichlorophosphoric acid monohydrate, $[PO_2Cl_2]^-[H_3O]^+$, was formed, again with loss of only 1 equivalent of hydrogen chloride. Pure dichlorophosphoric acid was said[354] to be unobtainable from partial hydrolysis of phosphoryl chloride, and a recent paper[355] by the same author gives the percentage of total phosphorus in the form of dichlorophosphoric acid (following addition of stoicheiometric amounts of alkali to ice-water hydrolysates) as:

| Mole ratio NaOH:$POCl_3$ | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| % Total P as $[PO_2Cl_2]^-$* | 93·1 | 93·3 | 44·4 | Nil |

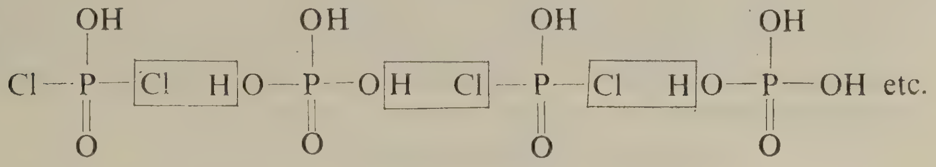
* By precipitation as the nitron salt $C_{20}H_{16}N_4HOPOCl_2$.

This is taken as indicative of 93% conversion to dichlorophosphoric acid in the untreated hydrolysate. Addition of an equimolar quantity of water to pure dichlorophosphoric acid followed by heating at 42°C. for 2 hr. gave a product with atom ratio Cl:P = 1·36; dichlorophosphoric acid (obtained as nitron salt) accounted for 68% of the total phosphorus, and the product contained no condensed phosphates as evidenced by paper chromatography. This is in accord with the composition: $0{\cdot}32H_3PO_4+0{\cdot}68H[PO_2Cl_2]+0{\cdot}36H_2O$. Both sets of results point to the complete absence of monochlorophosphoric acid, the further hydrolysis of which must proceed at a rate faster than its rate of formation. The hydrolysis of phosphoryl chloride is therefore expressed[355] by the two equations:

$$\begin{aligned} POCl_3+H_2O &= H[PO_2Cl_2]+HCl \\ H[PO_2Cl_2]+2H_2O &= H_3PO_4+2HCl \end{aligned}$$

In a similar study, at NaOH:$POCl_3$ mole ratios 1:1 to 0·01:1, only orthophosphate and a trace of pyrophosphate could be detected at the highest ratio. At lower ratios viscous liquid phases were formed, which contained in addition to ortho- and pyrophosphate, higher polyphosphates and trimetaphosphate.[520]

Paper chromatographic evidence following slow addition of an equimolar quantity of water to phosphoryl chloride over 14 days and subsequent evacuation of the hydrogen chloride and phosphoryl chloride at 60°C., showed[356–8] the presence of ortho-, pyro-, cyclic trimeta- and small amounts of polyphosphoric acids. With mole ratio $[H_2O]:[POCl_3]$ between 1:1 and 2:1 and subsequent heating under reflux at 80° to 100°C. for 30 min. or holding at room temperature for 6 months, cyclic trimeta- and polyphosphoric acids containing up to 9 phosphorus atoms were detected.[359] The mechanism was considered to be one of successive condensation between a chlorine atom of the dichlorophosphoric acid first formed (or of a higher condensed product) and a hydroxyl radicle of phosphoric acid (or of higher condensed products) with formation of P–O–P linkage and elimination of hydrogen chloride, according to the general scheme:



$$Cl-\overset{OH}{\underset{O}{P}}-\boxed{Cl\quad H}O-\overset{OH}{\underset{O}{P}}-O\boxed{H\quad Cl}-\overset{OH}{\underset{O}{P}}-\boxed{Cl\quad H}O-\overset{OH}{\underset{O}{P}}-OH \text{ etc.}$$

Using purely nuclear magnetic resonance methods on the products *in situ*, thereby avoiding such condensation and degradation changes as were shown[360] to be inherent in the analytical procedures earlier employed in this field, sealed tube equilibration of phosphoric acid–phosphoryl chloride mixtures (for 60 days at 25°, or 5 days at 110°C.) was shown to give[361] the following products at the listed phosphoryl chloride concentrations:

$>50$ mole %, dichlorophosphoric acid as the main product,
50 mole %, a small amount only of dichlorophosphoric acid,
$<60$ mole %, hydrogen chloride + condensed species containing $O_{1/2}PO(OH)_2$, $O_{1/2}P(OH)Cl$ and $O_{1/2}POCl_2$ end-groups, and $O_{1/2}PO(OH)O_{1/2}$ middle groups,
15–60 mole %, some hydrogen chloride as a separate liquid phase.

The results conform with those expected for a randomly reorganizing system, theory for which predicts essentially pure dichlorophosphoric acid at a mole ratio $POCl_3:H_3PO_4=2$. At the above ratio, as in the products from reaction of equimolar amounts of phosphoryl chloride in ether with water at room temperature, or of equimolar amounts of phosphoryl chloride with water at $-20°$ to $-10°$C., or of equilibration at 250°C. of such mixtures as required by the equations:

$$P_4O_{10}+6H_2O+8POCl_3 \rightarrow 12HO.POCl_2$$

and

$$P_4O_{10}+6PCl_5+5H_3PO_4 \rightarrow 15HO.POCl_2$$

$93 \pm 3\%$ of the total phosphorus was shown[361] to be present as dichlorophosphoric acid, and $7 \pm 3\%$ as condensed products. Hydrolysis rate measurements for both phosphoryl chloride and phosphorus(III) chloride in toluene at 25° and 35°C. were in conformity with pseudo mono-molecular reactions.[362] The data:

| | $K_v$ (sec.$^{-1}$) 20°C. | $K_v$ (sec.$^{-1}$) 35°C. | Activation energy (kcal. mole$^{-1}$) |
|---|---|---|---|
| $POCl_3$ | 0·018 | 0·037 | 8·396 |
| $PCl_3$ | 0·093 | 0·130 | 3·992 |

were taken as indicative of a semipolar P → O bond in phosphoryl chloride.

In the vapour phase at 25°C., hydrolysis of phosphoryl chloride was shown[113] to proceed by a wall reaction for which the rate of adsorption of water vapour on the phosphoric acid deposited on the walls of the vessel is the rate controlling step. With phosphorus(III) chloride vapour under similar conditions no reaction occurs. More recently[363] conductimetric, potentiometric and acid-base titration methods used in conjunction with a 'stopped-flow' procedure, by which separate dioxan solutions of phosphoryl chloride and water introduced simultaneously into a reaction vessel could be conveniently titrated at measured time intervals, have confirmed for the complete hydrolysis in the liquid phase:

(i) an initial fast reaction ($t_{1/2} = 10^{-2}$ sec.) corresponding to the production of two protons for each chloride ion and the formation of dichlorophosphoric acid:

$$\mathrm{H_2O + POCl_3 \rightarrow HO.POCl_2 + HCl}$$

(ii) a succeeding slow reaction ($t_{1/2}$ approx. 250 sec.) with development of one proton for each chloride ion, unaffected by acidity change between pH 4 to 7 and hence considered to involve the dissociated acid. Moreover, since the reaction rate remains unchanged in the presence of sodium phenoxide or nitrite (both reactive towards phosphorylating agents) but is increased by pyridine, the hydrolysis is thought to proceed through a bimolecular mechanism thus:

$$\begin{tikzcd}
\mathrm{HO.POCl_2} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Cl_2PO_2^- + H^+} \arrow[rd, "+\mathrm{H_2O}"'] & \\
 & & \mathrm{HCl + HO.PClO.O^-}
\end{tikzcd}$$

The rate of removal of the second Cl-atom is considerably faster than that of the first (in direct contrast to the corresponding fluoro acids), and of the following possible mechanisms:

$$\begin{tikzcd}
\mathrm{H^+ + HO.PClO.O^-} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, "+\mathrm{H_2O}"] & \mathrm{PClO(O^-)_2 + 2H^+} \arrow[ld, "+\mathrm{H_2O}"'] \arrow[d] \\
\mathrm{H_3PO_4 + HCl} & \mathrm{PO_3^- + Cl^-} \arrow[l, "+\mathrm{H_2O}"]
\end{tikzcd}$$

the route through unstable $PO_3^-$ is considered to be the more probable. At lower water contents, rapid reactions are thought[363] to occur as follows:

$$\begin{tikzcd}
\mathrm{POCl_3 + H_2O} \arrow[r] & \mathrm{HO.POCl_2 + HCl} \arrow[d, shift left] & & \\
 & \mathrm{H^+ + Cl_2PO_2^-} \arrow[u, shift left] \arrow[r, "+\mathrm{POCl_3}"'] & \mathrm{Cl_2PO.OPOCl_2} \arrow[r, "+\mathrm{H_2O}"'] & \mathrm{2HO.POCl_2}
\end{tikzcd}$$

This scheme leads initially to mixtures with dichlorophosphoric acid and pyrophosphoryl chloride as main components. Subsequent slower reactions result from the dissociation of the dichlorophosphoric acid, whence dichlorophosphate anions react with pyrophosphoryl chloride or the undissociated acid thus:

$$\mathrm{Cl_2PO_2^- + Cl_2PO.OPOCl_2 \rightarrow Cl_2PO.OPOCl.OPOCl_2 + Cl^-}$$
$$\mathrm{Cl_2PO_2^- + Cl_2PO.OH \rightarrow Cl_2PO.OPOCl.OH + Cl^-}$$

Further such P–Cl fission reactions, with corresponding release of hydrogen chloride, lead to longer straight chain or to cyclic species in a manner similar to that already described.[356, 359] Five-co-ordinate intermediates, in which the entering oxygen atom is transiently equivalent to the phosphoryl oxygen atom, have been postulated in the hydrolysis of some phosphate esters. However, the hydrolysis of phosphoryl chloride in water enriched with $^{18}O$ gave phosphoric acid containing three quarters of the $^{18}O$ concentration of the original water. Such intermediates can therefore have no part at any stage in the hydrolysis of phosphoryl chloride.[521]

Hydrolysis of phosphoryl chloride in sodium bicarbonate buffer solutions containing sodium phosphite or tetrasodium hypophosphate, has led[110, 364] to the isolation of salts of $P^3$–O–$P^5$ and $P^5$–O–$P^4$–$P^4$ acids, viz.: $Na(HO)PO.OPO(ONa)_2$, isohypophosphoric acid, and $(NaO)_2PO.OPO(ONa).PO(ONa)_2$, respectively (see Section XIX).

MISCELLANEOUS REACTIONS

Passing phosphoryl chloride vapour–hydrogen mixtures through an electrodeless discharge at room temperature gave[1] small amounts of elemental phosphorus and unidentified liquid products. Liquid hydrogen sulphide is slowly oxidized by phosphoryl chloride.[365] Fluorination occurs in liquid sulphur dioxide solution, slowly with nitrosyl fluoride,[366] or more conveniently with potassium fluoride.[122] Fluorination of phosphoryl chloride is discussed under phosphoryl fluoride; typical halogen exchange occurs with ammonium fluoride,[130] benzyl fluoride,[367] etc., and, where conditions permit repeated recycling of intermediate compounds, the product is wholly phosphoryl trifluoride. Phosphoryl chloride dissolves in absolute nitric acid to give a strongly yellow solution, the evaporation of which at 40°C. under reduced pressure was said[368] to afford a convenient preparation for metaphosphoric acid. The following mechanism was proposed:

$$\begin{aligned} POCl_3 + 3HNO_3 &= PO(NO_3)_3 + 3HCl \\ 3HCl + HNO_3 &= 2H_2O + Cl_2 + NOCl \\ PO(NO_3)_3 + 2H_2O &= 3HNO_3 + HPO_3 \\ \hline POCl_3 + HNO_3 &= HPO_3 + Cl_2 + NOCl \end{aligned}$$

Dinitrogen tetroxide in oxygen is strongly absorbed by phosphoryl chloride at −20°C. giving red solutions, which after distillation of gaseous products deposit colourless crystals of composition $P_2O_6NCl_2$.[138] Small amounts of pyrophosphoryl chloride are also formed. The crystals, separable under moisture-free conditions, decompose *in vacuo* at 50°C. leaving a darkish residue of resinous appearance and containing no nitrogen. Reaction with anhydrous ammonia at 70° to 100°C. leads to chlorine-free products consisting of mixtures of phosphoryl triamide, phosphoryl imidoamide and polyphosphorylamide (cf. Mellor, VIII, 1024). Numerous references[369–77] in the patent literature deal with the preparation, purification and subsequent heat treatment of these compounds, and with their application as flameproofing agents for cellulosic materials. Phosphoryl chloride, thiophosphoryl chloride and phosphorus(III) chloride have each been shown[378] to undergo largely similar type condensation reactions with methyl-, ethyl- and *tert.*-butylamines. With phosphoryl chloride, reaction to $PO(NHR)_3$ could be effected at 0°C. in petroleum ether; the methyl compound underwent thermal condensation to the imide $[P_2O_2N_3(CH_3)_3]_n$, but no such compound could be characterized from the *tert.*-butyl derivative.

Phosphoryl chloride is a more active inhibitor of the combustion of carbon than is carbon tetrachloride; comparative threshold concentrations are 1/2000 and 1/100 v/v., respectively.[379] Controlled combustion experiments at 750° to 1100°C. with differing carbons showed an increase in the $CO/CO_2$ ratio and in the oxygen content of the exit gases, when the incoming air-streams contained up to 2 v/v. % of various halide inhibitors. The effect was greatest[380] with phosphoryl chloride and phosphorus(III) chloride, i.e. those substances having a strong affinity for water at high temperatures. Comparative $CO/CO_2$ ratios at 850°C., each with the inhibitor in excess of its threshold concentration, were:

| inhibitor (<1%) | $POCl_3$ | $PCl_3$ | $Cl_2$, $CCl_4$,<br>$CHCl_3$, $SnCl_2$ | $CH_2Cl_2$,<br>HCl |
|---|---|---|---|---|
| mole ratio $CO/CO_2$ | 8·4 | 6·4 | 2·9–2·1 | 1·1 |

High activity has been linked[381] with high polarity, but from the above and similar experiments[380, 382–6] the ability to remove those species which are potential propagators of reaction chains, together with the thermal stability of the end product $(HPO_3)_x$, appear to be important factors. Combustion of coals was inhibited by the presence of approximately 1 v/v. % $POCl_3$ in the air-stream,[387] the net effect being a decrease in the ease of reaction with oxygen, and a short-lived acceleration followed by a depression of the reaction with carbon dioxide to give carbon monoxide. Chemical reaction between inhibitor and the coal surface was postulated. The effect of <2 v/v. % phosphoryl chloride vapour on the gasification of various coals in carbon dioxide was twofold[388]: (i) a reversible effect, initially catalyzing the reaction and almost independent of the nature of the coal, and (ii) an irreversible inhibiting effect, appearing only in strongly graphitized coals. The presence of carbon tetrachloride vapour decreases and that of phosphoryl chloride vapour rapidly increases the minimum partial pressure of oxygen at which chemiluminescence of white phosphorus begins.[389] The upper explosive limit of hydrogen–air mixtures, viz.: 74:26, is reduced to 64:36 in the presence of 5 mm. partial pressure phosphoryl chloride vapour; comparative figures are available for a number of compounds,[390] but the lower limit (11:89) is barely affected by any of them.

### COMPLEX FORMATION

There is a wide range of complex compounds in which phosphoryl chloride acts as a donor molecule towards other inorganic halides.[522] A calorimetric study showed that the heats of solution of acceptor chlorides in phosphoryl chloride were of the order 10–20 kcal./mole, and the heats of solution of the solvates 1–2 kcal./mole. Heats of solvation were found to be 8–23 kcal./mole for one co-ordination position (neglecting heats of vaporization and sublimation) and decreased in the order $SbCl_5 > FeCl_3 > AlCl_3 > \frac{1}{2}TiCl_4 > \frac{1}{2}SnCl_4 > GaCl_3 > BCl_3$.[523] Conductivity measurements in nitrobenzene solution point to the existence of zirconium and hafnium complexes of general formulæ $MCl_4,2POCl_3$ and $MCl_4,POCl_3$.[391] The compositions coincide with maxima at 184·7° and 205°C. (zirconium), 198·3° and 221·8°C. (hafnium), in the respective fusion diagrams.[392–3] Such diagrams failed to provide evidence for the compounds $2ZrCl_4,POCl_3$ and $3ZrCl_4,2POCl_3$ described by other authors.[246, 394–5] The 1:2 compounds begin to decompose above 60°C., the 1:1 compounds sublime at 130°C. and decompose above 145°C.[396] The 3:2 compounds: b.p. 360° (Zr), 355°C. (Hf), vapour pressure ratio 1·14 at the boiling point, heat of vaporization $20{\cdot}5 \pm 0{\cdot}05$ kcal. mole$^{-1}$,[394] were thought,[395] on evidence of non-uniform melting, to be azeotropic mixtures. Thus for the crystallized zirconium complex, melting at 98° to 100° (initial), 170° to 175° (bulk) and 225° to 230°C. (final crystals) was observed, while vapour density measurement at the boiling point indicated an average mol. wt. of about 450. For the 1:1 and 1:2 compounds in nitrobenzene solution, freezing point measurements[397] showed the former compound to be monomeric and the latter to dissociate to the monomer and phosphoryl chloride. Largely similar *X*-ray powder diagrams were obtained for the corresponding 1:1 and 1:2 zirconium and hafnium compounds; each, however, indicated a lower order of symmetry than the respective tetrahalides.[397, 524] Fractionation of the zirconium and hafnium complexes can be effected in multiplate columns,[394, 398] and recovery of the metals from the separated complexes is the subject of numerous patents.[247, 399]

The fusion diagram for the aluminium chloride–phosphoryl chloride system appeared to show a well-defined maximum at 186·5°C. corresponding to the 1:1 compound, and a 1:2 compound ($AlCl_3,2POCl_3$), m.p. 164°C., close to the eutectic between them. Further, by rapid cooling to −70°C. of the glassy non-crystalline material in the composition range 76–90 mole % $AlCl_3$, followed by slow warming to room temperature, leaflet crystals of a 1:6 complex ($AlCl_3,6POCl_3$), m.p. 41° to 42°C.[400–1] were obtained. Later authors have confirmed the existence of the 1:1 compound, m.p. 187–188°[422, 432, 525–7] with a heat of fusion of 14·3 kcal./mole.[533] However, although the 1:2 compound has also been subsequently reported,[526] it seems more likely to have the formula $2AlCl_3,3POCl_3$, and melts, possibly incongruently, at 188°C.[422, 527] No sign of the 1:6 compound could be detected in a thermal analysis of the $AlCl_3$–$POCl_3$ system.[527] $AlBr_3,POCl_3$ (m.p. 142° (decomp.)) is known,[526] as are the complexes $MgBr_2,2POCl_3$ and $MgBr_2,3POCl_3$.[542] Thermal analysis of the antimony(V) chloride–phosphoryl chloride system[402] gave 1:1 and 1:2 compounds, m.p. 150°C. (cf. 116°C.[403]) and 88·5°C. (incongruently with formation of 1:1 compound), respectively. Electrolysis of aluminium chloride or antimony(V) chloride solutions in phosphoryl chloride has shown[404] the presence of $AlCl_4^+$ and $SbCl_6^-$ ions with transport numbers $0{\cdot}04_4$ and $0{\cdot}05_0$, respectively; the relatively high migration velocities can be explained on the basis of chloride-ion transitions between $POCl_3$ molecules and $POCl_2^+$ ions. Raman evidence,[405–6] both from a saturated solution of antimony(V) chloride in phosphoryl chloride and from the crystalline 1:1 complex, confirmed the presence of $SbCl_6^-$ ions, and showed none of the characteristic frequencies for $SbCl_5$ molecules. Single crystal *X*-ray studies[407–8] (crystals prepared by a zone-melting technique in sealed capillaries) show the crystalline 1:1 complex to consist of orthorhombic unit cells of 4 mols., space group *Pmnb*, with $a = 8{\cdot}06$, $b = 16{\cdot}42$ and $c = 8{\cdot}93$ Å. There is octahedral co-ordination around the Sb atom with an O atom from $POCl_3$ at the sixth corner; the approximate tetrahedral structure of the $POCl_3$ molecule is preserved; the angle Sb–O–P is 143·7°. Refined data for this structure, as well as for the isostructural compounds $SbCl_5,OPMe_3$ and $NbCl_5,OPCl_3$, have recently been published.[409] Complex formation with phosphoryl chloride has been proposed[410] for the removal of aluminium chloride from Friedel–Crafts mixtures where separation as aluminium hydroxide is precluded by the presence of easily hydrolyzed chloride in the product, e.g., in the preparation of phenyldichlorophosphine, $PhPCl_2$. The solubility of the 1:2 complex ($AlCl_3,2POCl_3$) in nitrobenzene is given[411] as 5·91, 7·25 and 8·63 g./100 g. at 25°, 30° and 40°C., respectively (but see reference 527). Dissociation to the 1:1 complex and phosphoryl chloride occurs; such solutions show absorption maxima at 6900–7200 Å. which are not observed with the separate components.[412]

Treatment of ferric chloride with excess of phosphoryl chloride at 95°C. and subsequent cooling give water-soluble red crystals of the 2:3 complex ($2FeCl_3,3POCl_3$). These lose phosphoryl chloride at 50°C. *in vacuo* giving yellow-brown crystals of the 1:1 complex. Other data[413] include:

| Complex | m.p. °C. | $\log_{10} p$(mm.) | Heat of dissociation (kcal. mole$^{-1}$) | Apparent mol. wt. in nitrobenzene |
|---|---|---|---|---|
| $2FeCl_3,3POCl_3$ | $98 \pm 0{\cdot}2$ | $11{\cdot}38 – 3225/T$ | 14·56 | 310 |
| $FeCl_3,POCl_3$ | $119 \pm 0{\cdot}2$ | $13{\cdot}53 – 4167/T$ | 18·16 | 344 |

The colour of ferric chloride solutions in phosphoryl chloride increases with concentration thus:

| $1 \times 10^{-5}$ M. | $1 \times 10^{-3}$ M. | 0·1 M. | 0·3 M. |
|---|---|---|---|
| colourless | yellow | dark red | dark brown |

The ultra-violet absorption spectra for $10^{-4}$ M. solutions before and after neutralization with tetraethylammonium chloride were similar to those of ferric chloride in concentrated hydrochloric acid, so indicating the presence of $FeCl_4^-$ ions and providing apparent evidence of self ionization of the solvent[414]:

$$FeCl_3 + POCl_3 \rightleftharpoons FeCl_4^- + POCl_2^+$$

However, electrolysis of a radioactive $^{59}FeCl_3$ complex with phosphoryl chloride showed that iron atoms were present in both cationic and anionic species possibly of the type $(POCl_3)_2FeCl_2^+.FeCl_4^-$, no $POCl_2^+$ ions being detected.[528] This is consonant with other evidence for compounds of the type $(Cl_3PO)_nMCl_x^+.MCl_{x+2}^-$.[422, 444, 529–31] Addition of carbon tetrachloride to the red (while hot) and to the yellow solutions above gives crystals of the 2:3 and 1:1 complexes, respectively. The colour change red → yellow occurs on addition of a chloride-ion donor, e.g. tetraethylammonium chloride, potassium chloride, etc.; for dilute, yellow solutions, the change is reversed on addition of a chloride-ion acceptor, e.g. antimony(V) chloride, or by concentrating.[415] Analogy with the antimony(V), tin(IV) and titanium(IV) chloride complexes shown from *X*-ray,[407–8, 416–7] infra-red[418–9] and Raman[405, 420–1] evidence to be oxygen-co-ordinated, leads to the conclusion[415] that the ferric and aluminium complexes are similarly co-ordinated in the solid state. The amphoteric and high conductance properties of aluminium chloride in phosphoryl chloride medium are explained[422] on the basis of ionization to $[AlCl_2(POCl_3)_2]^+[AlCl_4]^-$. In the presence of polar chlorides, $AlCl_4^-$ ions are formed; but with strong chloride-ion acceptors, solvated $AlCl^{++}$ ions may be present, or insoluble complexes such as $[Al(OPCl_3)_6][SbCl_6]_3$ are precipitated.[423]

Molecular 1:1 and 1:2 compounds (m.p. 104°, 105·7, and 105°C., respectively) have been identified in the titanium(IV) chloride–phosphoryl chloride system[424–5, 524–5, 532] and a 1:2 compound (m.p. 59°, b.p. 117°C.) in the tin(IV) chloride–phosphoryl chloride system[425, 524]; a proposed extraction route for titanium metal consists[426] of causing the 1:1 complex, $TiCl_4,POCl_3$ (formed by refluxing the chlorides together in stoicheiometric proportions) to react with sodium–potassium alloy or with mercury, and distilling the resulting titanium amalgam. The compounds are completely dissociated above 80°C. (above 60°C. for $SnCl_4,2POCl_3$) in the vapour phase, the O–Ti bond energy of the titanium complex being only 6·4 kcal./mole.[532] For $TiCl_4,2POCl_3$, $\log_{10} p_{(mm.)} = 8{\cdot}914 - 2523/T$, specific conductivity at 105°C. (molten state) $= 0{\cdot}138 \times 10^{-2}$ mho cm.$^{-1}$, $d_4^t = 2{\cdot}1027 - 3{\cdot}013 \times 10^{-3}t$ and the molar volume at 100°C. is 275·6 ml. (cf. 319·6 ml. for the components). Molar contraction was also observed for the $SnCl_4,2POCl_3$ complex at 100°C., viz., 315·6 ml. against 327·6 ml. for the components,[425] but parachor considerations[427] showed the latter compound to be largely dissociated in the liquid state. The b.p. (100 mm.) was 70°C., m.p. 54·5°C. and $d_4^t$ $2{\cdot}090 - 0{\cdot}00293t$. It was suggested[425] (in agreement with the conclusions[406] from a Raman study of the compound $SbCl_5,POCl_3$) that these compounds are co-ordination complexes with chlorine acting as the donor atom. However, other considerations,[250, 420, 428] but primarily the shifts in the infra-red P → O stretching frequency resulting from adduct formation[418, 532] and *X*-ray crystal analysis,[417, 429] assign them as oxygen-coordinated in the solid state. The $TaCl_5,POCl_3$ crystal, orthorhombic, space group *Pnma*, $a = 16{\cdot}4$, $b = 8{\cdot}1$, $c = 9{\cdot}0$ A. is isostructural with $SbCl_5,POCl_3$, and the $TiCl_4,2POCl_3$ crystal, orthorhombic, space group *Pnnm*, $a = 13{\cdot}4$, $b = 13{\cdot}5$, $c = 7{\cdot}7$ A. is isostructural with $SnCl_4,2POCl_3$.[417] This stannic 1:2 complex, $a = 14{\cdot}53 \pm 0{\cdot}02$, $b = 14{\cdot}25 \pm 0{\cdot}05$, $c = 8{\cdot}01 \pm 0{\cdot}01$ A., 4 mols./unit cell, has an octahedrally co-ordinated Sn atom with two $POCl_3$ groups (crystallographically different, though preserving their approximately tetrahedral structure) lying in *cis* position, the O-atoms in each group functioning as donor atoms.[429] The 1:1 titanium chloride–phosphoryl chloride crystalline complex is built up of dimeric molecules $(TiCl_4,POCl_3)_2$ with two chlorine bridges between octahedrally co-ordinated titanium atoms, the oxygen atoms in each $POCl_3$ group functioning as donor atoms.[416]

Mixed halide systems containing titanium(IV) chloride and phosphoryl chloride have been described. These include $TiCl_4,NbCl_5,3POCl_3$ (m.p. 96°C.), $TiCl_4,TaCl_5,POCl_3$ (m.p. 113·5°C.),[533–4] and $TiCl_4,SbCl_5,3POCl_3$ (probably $TiCl_3(OPCl_3)_3{}^+SbCl_6{}^-$).[535] Similar mixed halide systems are formed by aluminium chloride, e.g. $AlCl_3,NbCl_5,3POCl_3$ (m.p. 198°) and $AlCl_3,TaCl_5,3POCl_3$ (m.p. 217·5°).[536] Oxyhalides of Groups IVa and Va also form complexes including $TiOBr_2,2POCl_3$,[537] $TiOCl_2,2POCl_3$,[538] $ZrOCl_2,2POCl_3$,[539] $Zr_2OCl_6,4POCl_3$ (probably $ZrCl_3(OPCl_3)_3{}^+ZrOCl_3(OPCl_3)^-$)[540] and $VOCl_3,2POCl_3$.[541]

In the gallium chloride–phosphoryl chloride system 1:1 and 1:2 compounds (m.p. 118·5° and 77°C., respectively) occur[430, 526] and a detailed comparison of physical properties of the former with those of its components at their respective melting points has been made.[430] Thus, at 118·5°C. the molar volume is 179·98 ml. (cf. 192·16 ml. for the components), specific conductivity $= 1{\cdot}26 \times 10^{-3}$ mho cm.$^{-1}$ (ca. $2 \times 10^{-6}$ for components), vapour pressure is $<1$ mm.,

$$d_4^t = 1{\cdot}8281 - [1{\cdot}526 \times 10^{-3}(t - 120)]$$

from 111° to 149°C., and the compound may be sublimed without decomposition.

Approximate values of % ionic dissociation at the melting points derived[430] from the molar conductances for molten gallium 1:1, and also for molten titanium and tin(IV) 1:2 complexes were:

| Complex | m.p. °C. | Molar conductance (mho cm.$^2$ mole$^{-1}$) | Ionic dissociation % |
|---|---|---|---|
| $GaCl_3,POCl_3$ | 118·5 | 0·227 | 0·5 |
| $TiCl_4,2POCl_3$ | 105 | 0·384 | 0·75 |
| $SnCl_4,2POCl_3$ | 55 | 0·025 | 0·05 |

Configurations implying electron donation from a Cl atom of $POCl_3$ to the metal atom were proposed for these compounds,[430] but in view of the later *X*-ray structural work[416–7] (described above) those for the titanium and tin compounds at least, must now be discounted. The measured $\Delta H$ for the reaction:

$$GaCl_3(c) + POCl_3(l) = GaCl_3,POCl_3(c)$$

at 25°C. was $-10·2$ kcal. mole$^{-1}$,[330] and values of $-22·6$ and 280·0 kcal. mole$^{-1}$ were derived for the heat of reaction in the gas phase and for the standard heat of formation from the elements ($\Delta H^\circ_{f_{25}}$), respectively. The complexes $InCl_3,POCl_3$ (m.p. $>250°$) and $TlCl_3,2POCl_3$ have been detected by infra-red and Raman spectroscopy.[526]

Maxima in the fusion diagrams for the respective binary systems correspond to complex formation as follows:

| Complex | m.p. °C. | Ref. |
|---|---|---|
| $AsCl_3,POCl_3$ | $-22$ to $-25$ | 403 |
| $BiCl_3,2POCl_3$ | 37 | 431 |
| $SnCl_4,2POCl_3$ | 55 to 57 | 403 |
| $SbCl_5,POCl_3$ | 115 to 117 | 403 |

but provide no evidence of the tin(IV) 2:1 and 1:1 compounds earlier described.[432] For the arsenic, antimony and bismuth(III) chloride systems, infra-red and Raman shifts vary in a continuous manner with mole ratio; for the tin(IV) and antimony(V) systems, spectra of free and bonded molecules were observed. It was tentatively concluded[421, 431] that the former complexes involve a dipole–dipole and the latter an electron pair interaction, but the true nature of the bonding awaits further structural information.

The 1:1 complexes with niobium or tantalum pentachlorides (m.p. 124·5° and 132·4°C., respectively) lose part of their phosphoryl chloride on heating to form sublimable residues of composition $POCl_3,1·49NbCl_5$ and $POCl_3,1·22TaCl_5$.[433–4, 536] However, they are said to be more stable than $TiCl_4,POCl_3$.[534] Distillation of the respective reaction mixtures used in the preparation of the 1:1 complexes gives similarly composed azeotropes.[435] Rectification of tantalum(V), niobium(V) and zirconium(IV) chloride mixtures in phosphoryl chloride can be effected at atmospheric pressure using a 20-plate fractionating column at reflux ratio = 15:1.[436] Recent *X*-ray structural work[409] shows $NbCl_5,POCl_3$ to be isostructural with both $SbCl_5,POCl_3$ and $SbCl_3,PO(CH_3)_3$; the space group is *Pmnb* with $a = 8·07 \pm 0·01$, $b = 16·23 \pm 0·03$, $c = 8·83 \pm 0·02$ A. Wide variation in the Nb–Cl bond lengths (comparable with that for the non-bridging bonds in $Nb_2Cl_{10}$) was observed.

The tetrasolvate complex $UCl_4,4POCl_3$ is precipitated as pale green tetragonal crystals, m.p. 340°C. (sealed tube), refractive indices $n_e$ 1·645, $n_o$ 1·657, from phosphoryl chloride solutions of uranium tetrachloride on standing. The crystals lose phosphoryl chloride on gentle heating *in vacuo* to give pale blue-green $UCl_4,POCl_3$, refractive indices 1·645, 1·660.[437]

Phosphoryl chloride is a convenient ionizing solvent for the chlorides of non-metals and of many transition elements, the solvo-system being the subject of an extensive literature including several review articles.[259, 428, 438] Self-ionization of the solvent occurs with chloride ion transfer: thus, an acid is defined as a chloride ion acceptor and a base as a chloride ion donor. The equilibrium:

$$2POCl_3 \rightleftharpoons POCl_2^+ + POCl_4^-$$

is temperature dependent, the graph of specific conductance against temperature showing a maximum at $2{\cdot}49\times10^{-6}$ mho cm.$^{-1}$ at 88°C.[343] The molar conductance of 0·001 M. alkali halide solutions in phosphoryl chloride increases with increase in the radius of the solute ions. The data at 20°C. (Table XI) show that these halides exhibit a slight to moderate degree of ionization in this solvent.[439] More recent measurements[324] in an inert atmosphere have given somewhat different results:

*Table XI.—Solubility-conductivity Data for Phosphoryl Chloride Solutions at* 20°*C.*

| Solute | Solubility (g./litre) | Specific conductance (mho cm.$^{-1}$) | Equivalent conductance (mho cm.$^2$ mole$^{-1}$) of 0·001 molal solutions |
|---|---|---|---|
| $POCl_3$ | — | $0{\cdot}155\times10^{-5}$ | — |
| LiCl | 0·05 | 0·66 ,, | 4·0 |
| NaCl | 0·31 | 3·0 ,, | 6·4 |
| KCl | ~0·60 | 3·4 ,, | 6·7 |
| $NH_4Cl$ | 0·46 | 3·6 ,, | 6·9 |
| RbCl | 0·87 | 8·3 ,, | 14·6 |
| CsCl | 1·20 | 11 ,, | 16·0 |
| $(CH_3)_4NCl$ | ~2·00 | 55 ,, | 37·6 |
| KF | ~0·40 | $2{\cdot}6\times10^{-5}$ | 6·4 |
| KBr | 0·51 | 4·3 ,, | 14·5 |
| KI | ~1·71 | 12 ,, | 23·1 |
| KCN | ~0·73 | 3·3 ,, | 7·2 |
| KCNO | ~0·80 | 3·1 ,, | 9·0 |
| KCNS | ~0·76 | 2·9 ,, | 6·6 |

| | Specific conductance (mho cm.$^{-1}$ at 20°C.) | Dissociation, $K$ |
|---|---|---|
| $POCl_3$ | $2\times10^{-8}$ | $\leq 9\times10^{-14}$ |
| $5{\cdot}97\times10^{-7}$ M. $(C_2H_5)_4NCl$ in $POCl_3$ | — | $7{\cdot}1\times10^{-4}$ |
| $5{\cdot}43\times10^{-2}$ M. $(C_2H_5)_4NCl$ in $POCl_3$ | — | |

In the above concentration range tetraethylammonium chloride behaves as a typical polar compound in a solvent of low dielectric constant; similar results were obtained[499] with tetrapropylammonium chloride, tetrabutylammonium chloride and tetraethylammonium bromide, iodide or perchlorate as solute. Evaluation of the limiting conductivities, dissociation constants, Bjerrum parameters and ionic mobilities from the conductimetric data[499] for these solutions and also for solutions of the tetra- and triethylammonium complexes with ferric chloride, antimony(V) chloride, etc.,[440] permitted treatment in terms of electron pair donor-acceptor and ion-pair equilibria of the Bjerrum type. With triethylamine, $Et_3N$, as solute, the overall equilibrium is expressed[441]:

$$Et_3N + POCl_3 \rightleftharpoons [Et_3NPOCl_2^+.Cl^-] \rightleftharpoons Et_3NPOCl_2^+ + Cl^-$$

the overall dissociation constant has the value $2{\cdot}6\times10^{-5}$. Dilute solutions of triethylammonium chloride in phosphoryl chloride contain approximately equal amounts of $Et_3NH^+$ and $Et_3POCl_2^+$ ions, the co-ordination affinity of protons for triethylamine being close to that of the ion $POCl_2^+$.[422]

Typical of the numerous solvate compounds which have been isolated are $SbCl_5,POCl_3$ and $TiCl_4,2POCl_3$. The former behaves as a monobasic acid and the latter as a dibasic acid in phosphoryl chloride solution.[442] A more recent conductimetric and potentiometric study of such solutions shows[443] that the dissociation:

$$SbCl_5,POCl_3 \rightleftharpoons POCl_2^+ + SbCl_6^- \qquad (K = 4\times10^{-6})$$

is basically dependent upon the equilibrium between chloride ion and the oxygen co-ordinated complex:

$$SbCl_6^- \underset{-POCl_3}{\overset{+POCl_3}{\rightleftharpoons}} Cl_5SbOPCl_3 + Cl^- \qquad (K \leq 10^{-9})$$

Thus, in such coupled equilibria, the co-ordinating tendency of phosphoryl chloride through oxygen exceeds its chloride ion donor strength. Titration of titanium(IV) chloride with tetraethylammonium chloride in phosphoryl chloride media suggests the acceptance of either 1 or 2 chloride ions with formation of $TiCl_5^-$ or $TiCl_6^{--}$. Titrations with ferric chloride or antimonic chloride, however, typify donation of a chloride ion from $TiCl_4$; formulations of type $[TiCl_3(OPCl_3)_3]^+[FeCl_4]^-$ have been suggested for these complexes.[444] Potassium and cæsium chlorides readily dissolve in phosphoryl chloride solutions of antimony(V) or iron(III) chloride, and ebullioscopy[338] in concentrations up to $10^{-3}$ M. shows that the soluble potassium chloride complexes $KSbCl_6$ and $KFeCl_4$ are 60 and 45% dissociated respectively. The degree of dissociation decreases rapidly with increasing concentration, but is somewhat greater than that derived conductimetrically[324, 443] for the salts of the larger tetraethylammonium cation in phosphoryl chloride solutions at room temperature.

Tetraethylammonium chloride, alkali metal chlorides, zinc chloride and phosphorus(V) chloride behave as solvo-bases in phosphoryl chloride solution, e.g.,

$$(CH_3)_4NCl + POCl_3 \rightarrow (CH_3)_4N^+ + POCl_4^- \text{ }^{445}$$

Addition of such solutions to red solutions of tungsten(VI) chloride in phosphoryl chloride gives yellow solvated complexes of the ion $WCl_7^-$, but these are stable only in the presence of the solvent.[446] Solid compounds containing the $POCl_4^-$ ion are not known.[428, 442] The reaction:

$$POCl_2.SbCl_6 + (CH_3)_4NCl \rightarrow (CH_3)_4NSbCl_6 + POCl_3$$

in phosphoryl chloride is typical of neutralization, and the resulting salt (soluble in phosphoryl chloride) is not obtainable directly from tetraethylammonium chloride and antimony(V) chloride.[442] Such neutralization affords a general preparative method for chloro-complexes[244, 445] which, where not insoluble, may be isolated by evaporation or by change of solvent. Thus, a 1:2 pyridine complex, $POCl_3,2C_5H_5N$, slightly soluble in phosphoryl chloride, is precipitated by addition of carbon tetrachloride.[447] Conductivity measurements at 20°C. give the dissociation constant for the equilibrium:

$$POCl_3,2C_5H_5N \underset{-POCl_3}{\overset{+POCl_3}{\rightleftharpoons}} 2[POCl_2,C_5H_5N]^+ + 2Cl^- \text{ as } 1{\cdot}34\times10^{-4}$$

The complex is solvo-basic and forms compounds of the type $[C_5H_5N,POCl_2]^+[MCl_6]^-$ with vanadium, antimony, tantalum or phosphorus pentachlorides. Potentiometric titration using a molybdenum electrode and antimony(V) chloride as titrant,[262] gave the order of basicity for various chlorides in phosphoryl chloride as:

$SbCl_5 < FeCl_3$ (acidic) $< ZrCl_4 < SbCl_3 < POCl_3 < SnCl_4 < TaCl_5 < NbCl_5 < AlCl_3 < PCl_5 < TiCl_4$ (amphoteric) $< (CH_3)_4NCl <$ pyridine $< (C_2H_5)_4NCl$ (basic)

In addition, vanadium(IV) chloride[248] and boron trichloride[448] behave as acids and the alkali chlorides[442] as bases. Typical comparative titrations against tetraethylammonium chloride and antimony(V) chloride followed potentiometrically, conductimetrically and by use of indicators[262] may be summarized:

| In $POCl_3$ solution | $(C_2H_5)_4NCl$ titrant | $SbCl_5$ titrant |
|---|---|---|
| $TiCl_4$ | 1:1 and 1:2 reactions corresponding to the formation of soluble acid and slightly soluble neutral salts, respectively. | 1:1 reaction. Solution deposits yellow crystals of $TiCl_3,SbCl_6,2POCl_3$ on standing. |
| $AlCl_3$ | 1:1 reaction. | 1:1 reaction. |
| $PCl_5$ | no break observed in the titration curves; white, fine crystals of $(C_2H_5)_4NPCl_6$ formed. | 1:1 reaction. |
| $FeCl_3$ | 1:1 reaction; voluminous white 'chloroferrate' precipitated. | no reaction. |

With 0·02–0·04 M. metal chloride solutions as titrants, potentiometric titration of 0·02 M. tetraethylammonium chloride in phosphoryl chloride[449] gave the order of decreasing acid strength as:

$$FeCl_3 > SbCl_5 > NbCl_5 > TaCl_5 > SnCl_4 > AuCl_3 > ZrCl_4 > TiCl_3 > AlCl_3 > TeCl_4 > TiCl_4$$

Each showed a break at the 1:1 equivalence point, weak for titanium, zirconium and tin chlorides, which also showed breaks at the 1:2 $MCl_4:(C_2H_5)_4NCl$ equivalence point. It was concluded[450–1] that the acidic or basic character of the solute is determined by its tendency towards co-ordination with chloride ion (acidic) or with oxygen of a phosphoryl chloride molecule (basic) according to the general equation:

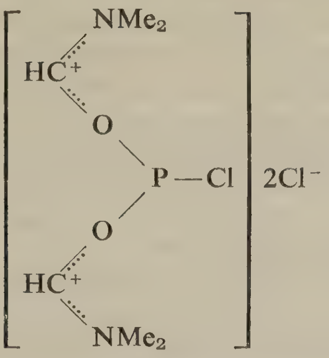
$$(MCl_{n+1})^- + POCl_2^+ \rightleftharpoons Cl_nMOPCl_3 \rightleftharpoons (MCl_{n-1},POCl_3)^+ + Cl^-$$

Spectrophotometric observation (400–600 mμ) of $FeCl_4^-$-ion formation in approximately 0·02 M. ferric chloride solutions has provided further evidence[452–3] of the order of basicity of chloride ion donor compounds in phosphoryl chloride. Thus basicity decreased in the sequence: $(C_2H_5)_4NCl$, KCl, $ZnCl_2$, $AlCl_3$, $AlCl_2^+ > TiCl_4 > PCl_5$, $AlCl^{++} \gg SbCl_6^-$, $HgCl_2 > BCl_3$, $SnCl_4$. Chloride ion transfer from phosphoryl chloride to ferric chloride is also facilitated by pyridine, triethylamine and tetraethylammonium bromide, chlorate or permanganate.[454]

Heat is absorbed on mixing phosphoryl chloride with sulphuryl chloride and observed vapour pressures for the system were higher than the values calculated from individual partial pressures.[455] However, the fusion diagram (eutectic −73·8°C.) provides no evidence of compound formation[456]; boiling point, density and viscosity data (the latter from 15° to 35°C.) are available.[457–8] Phosphoryl chloride is miscible in all proportions with liquid sulphur dioxide[119] and chlorine[329]; thermal analysis of the second system shows the formation of a compound, $2POCl_3,Cl_2$, which forms yellow prismatic crystals, decomposing above −55°C.[329]

Heats of solution for inorganic oxychlorides in chloroform were taken[459] as a measure of C–H ← O bonding. For phosphoryl chloride the heat evolved was 0·48 kcal. mole$^{-1}$, in reasonable agreement with a value of 2 kcal. mole$^{-1}$ estimated from Raman data,[543] and, as a general rule, the presence of halogen in the donor molecule was accompanied by decrease in the bonding strength. Infra-red spectra for such solutions[460] have confirmed the order of hydrogen bonding as $OP(n\text{-}C_4H_9)_3$

$> OP(C_2H_5)_3 > OPCl_3$. A complex of dimethylformamide with phosphoryl chloride, $POCl_3,2DMF$ has been isolated, and assigned the structure[544]



The stability constant and enthalpy of formation of a 1:1 complex between Crystal Violet and phosphoryl chloride have been determined.[545]

Phosphoryl chloride is readily soluble in liquid hydrogen chloride and in such solutions behaves as a base of medium strength, the specific and molar conductance of a 0·48 M. solution being $9{\cdot}35 \times 10^{-5}$ mho $cm.^{-1}$ and 0·20 mho $cm.^2$, respectively. The ionization is believed to be expressed by:

$$POCl_3 + HCl \rightleftharpoons POCl_2^+ + HCl_2^-$$

and conductimetric titration with boron trichloride or trifluoride shows a break at the 1:1 mole ratio. The solid adducts are isolated on evaporation of the solvent (m.p. $POCl_3,BF_3 = -3$°C. with decomposition) and infra-red evidence confirms co-ordination through oxygen to the boron.[263–5, 461] Similar evidence[526] supports the existence of other adducts with the properties shown below:

| Property | Ref. | $BCl_3,POCl_3$ | $BBr_3,POCl_3$ | $BCl_3,POBr_3$ | $BBr_3,POBr_3$ |
|---|---|---|---|---|---|
| m.p. °C. | 526 | 73 | 128 | — | 150 |
| | 546 | 72–75 | 126–129 | 115–118 | 152–154 |
| $\Delta H^{(a)}$ kcal./mole | 546 | $-40{\cdot}2^{(b)}$ | $-50{\cdot}8$ | $-35{\cdot}0$ | $-33{\cdot}7$ |

$^{(a)}$ Defined by the equation $POX_3(g) + BY_3(g) = POX_3,BY_3(c)\ \Delta H$.

$^{(b)}$ A value of 26·1 kcal./mole derived[546] from earlier data[463] suggests the existence of two forms of this complex.

Rapid isotopic exchange between $^{36}$Cl-labelled boron trichloride and excess of phosphoryl chloride at 0°C. is also interpreted[462] in terms of co-ordination through oxygen:

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$$
$$Cl^- + Cl_3^*B.OPCl_3 \rightleftharpoons [Cl_4^*B.OPCl_3]^- \rightleftharpoons Cl^{*-} + Cl_3B.OPCl_3$$

An approximate value for the free energy of dissociation of the last complex is $\Delta G^\circ_{298} = -4{\cdot}6$ kcal. $mole^{-1}$.[463]

Phosphoryl chloride gives slightly conducting solutions in tin(IV) chloride and behaves as a solvo-base in titrations against antimony(V)-, arsenic(III)- and iodine-chloride solvo-acids.[464]

Electrolysis of saturated phosphoryl chloride in triethylammonium chloride solution using platinum electrodes gave[465] chlorine at the anode and a brownish solid of composition $(PO)_n$ at the cathode. The following equations are suggested:

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$$
$$3n[POCl_2]^+ \rightleftharpoons [PO]_n + 2nPOCl_3$$

The solid is insoluble and stable in water. It gives phosphine with alkali, and its composition has been verified by controlled oxidation to phosphorus pentoxide at 300°C.

## PHOSPHORYL CHLOROBROMIDES

The mixed phosphoryl halides are obtained by the reaction of phosphorus(V) dibromotrichloride with acetic acid, or of phosphorus pentachloride–pentabromide mixtures with acetic acid, alcohols or acetone.[466] By equilibrating equimolar phosphorus trichloride–tribromide mixtures at 140°C., cooling and reacting first with bromine and then with phosphorus pentoxide,[467] a product is obtained which can be decanted from unreacted pentoxide and separated into the various mixed halides by fractional distillation at reduced pressure. Small quantities of both chlorobromides also arise during the thermal decomposition of the complex $MgBr_2,3POCl_3$ in the presence of excess phosphoryl chloride.[542]

Phosphoryl dichlorobromide is a water-white liquid, b.p. 52° to 53°C. (39 mm.), 135°C. (758 mm. Hg), giving colourless crystals, m.p. 10° to 11°C. It fumes in moist air and is not decomposed by distillation at normal pressures. The dibromochloride forms as colourless crystals, m.p. 31°C., which rapidly assume a bromine coloration in moist air. Boiling points are 49°C. at 12 mm., 165°C. at 759 mm. Hg.[467] Fluorination proceeds with powdered antimony(III) fluoride at 80°C. (100 mm. pressure) to give small amounts of phosphoryl monofluorochloride, monofluorobromide and fluorochlorobromide condensing at −60°C. The last compound, (POFClBr), has b.p. 79° to 80°C., *d* 1·87, and a Raman spectrum typical of a tetrahedral structure devoid of any symmetry element.[466]

## PYROPHOSPHORYL CHLORIDE, $P_2O_3Cl_4$

### Preparation

Pyrophosphoryl chloride is conveniently prepared by passing chlorine into a boiling suspension of phosphorus pentoxide in phosphorus trichloride diluted with carbon tetrachloride. Phosphorus pentachloride forms *in situ*, and its subsequent reaction can be written:

$$P_4O_{10}+4PCl_5 = 2P_2O_3Cl_4+4POCl_3$$

Maximum yields (30% on the total P) are obtained with a reactant mole ratio $P_4O_{10}:PCl_3 = 1:4$, and experiments using $^{32}P$-labelled phosphorus trichloride have confirmed that the P–O–P linkage originates from the phosphorus pentoxide.[468] The reaction between phosphorus trichloride and nitrogen tetroxide at −10°C. (Mellor, VIII, 1027) has been reinvestigated.[138] The main products (yields based on $PCl_3$) were said to be phosphoryl chloride 58%, pyrophosphoryl chloride 17%, tetraphosphoryl decachloride 6% and colourless crystals of composition $P_2O_6NCl_2$ 14%. A free radicle mechanism was proposed:

$$Cl_3P+ONO \rightarrow Cl_3\dot{P}ONO \rightarrow Cl_2\dot{P}O+NOCl$$

$$Cl_2\dot{P}O+ONO \rightarrow Cl_2PO.O\dot{N}O \xrightarrow{+\dot{P}OCl_2} Cl_2PO.OPOCl_2+NO$$

Yields of 17% and 12%, respectively, can be obtained by controlled addition of 1 mole of water to a vigorously stirred solution of 2 moles of phosphoryl chloride in carbon tetrachloride,[469] or to 1 mole of phosphoryl chloride at 0°C.[470] The last traces of hydrogen chloride, diluent and unreacted phosphoryl chloride are removed at 60° to 90°C. under vacuum. Pyrophosphoryl chloride separates at 110° to 135°C. and is purified by redistillation under high vacuum at 66° to 70°C. Other authors,[98] however, showed that the reaction between 1 mole of water and 1 mole of phosphoryl chloride at −20° to −10°C. gives dichlorophosphoric acid; heating at 100°C. gave an upper layer of phosphoryl chloride, and a lower layer which on further heating gave pyrophosphoryl chloride. A 30% conversion to pyrophosphoryl chloride (based on total P) was achieved[471] from fractional distillation of the products of the sealed tube reaction between phosphoryl chloride and phosphorus pentoxide at 200°C. (optimum mole ratio $POCl_3:P_2O_5 = 3–4:1$). Dichlorophosphoric acid (obtained in 90 to 97% purity either by warming 1 mole of phosphoric acid with 2 moles of phosphoryl chloride,[474] by low temperature hydrolysis of pyrophosphoryl chloride,[354, 472–3, 475] or by reorganization of other suitable mixtures in sealed tube reactions[361] (see page 493) undergoes 35% conversion to pyrophosphoryl chloride, either on addition to excess phosphoryl chloride at 90°C. and vacuum fractionation[474, 476] or by condensation at 100°C. and 12 mm. pressure in a current of hydrogen chloride.[354, 472–3] The above reactions may be expressed:

$$H_3PO_4 + 2POCl_3 \rightarrow 3HOPOCl_2$$
$$HO.POCl_2 + POCl_3 \rightarrow P_2O_3Cl_4 + HCl$$

The dehydration reaction:

$$2HO.POCl_2 \rightarrow P_2O_3Cl_4 + H_2O$$

proceeds only at 300°C. in the absence of hydrogen chloride.[354, 472] Addition of 1 mole of phosphorus(V) chloride to 2 moles of dichlorophosphoric acid followed by vacuum fractionation gives better than 90% conversion to pyrophosphoryl chloride.[477–8, 547] The following mechanism is postulated[477]:

$$PCl_5 + 2HO.POCl_2 \rightarrow Cl_3P(OPOCl_2)_2 + 2HCl$$
$$\hookrightarrow POCl_3 + P_2O_3Cl_4$$

With cyanogen chloride under reflux, the following reaction occurs[479]:

$$2HO.POCl_2 + ClCN \rightarrow P_2O_3Cl_4 + ClCONH_2$$

### Properties

Pyrophosphoryl chloride is a colourless, oily, strongly refractive liquid, $d_4^{15}$ 1·820, b.p. 65°C. at 1 mm., 210° to 215°C. with decomposition at 760 mm. Hg,[138] m.p. $-16{\cdot}5$°C.[471] Raman evidence[480] confirms the presence of two $O{:}PCl_2$ groups connected by an oxygen bridge. The pure liquid is odourless and does not fume in air; it is soluble in inert organic solvents and reacts with amides and alcohols. The hydrolysis reaction with water is vigorous and comparable with that of phosphoric anhydride.[138] Controlled hydrolysis, by dropwise addition of an equimolar quantity of water to pyrophosphoryl chloride at $-70$° to $-60$°C. with stirring, gives dichlorophosphoric acid in a strongly exothermic reaction.[354, 472, 475] With saturated ammonia in ether or chloroform solution at $-25$°C. the products of reaction are dependent upon the availability of water,[481] thus:

(i) in dry solvent:

$$Cl_2PO.OPOCl_2 + 8NH_3 \rightarrow (H_2N)_2PO.OPO(NH_2)_2 + 4NH_4Cl$$

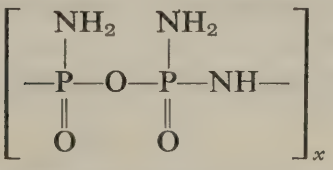
(ii) in the presence of 0·01% $H_2O$:

$$Cl_2PO.OPOCl_2 + 9NH_3 \rightarrow (H_2N)_2PO.NH_2 + HO.PO(NH_2)_2 + 4NH_4Cl$$

(iii) in the presence of 0·05 to 1% $H_2O$

$$Cl_2PO.OPOCl_2 + 10NH_3 + H_2O \rightarrow 2(NH_2)_2PO.ONH_4 + 4NH_4Cl$$

Filtration followed by washing with liquid ammonia until free from chloride ion gives approximately 90% yields for reactions (i) and (iii). Tetramidodiphosphate, product of reaction (i), is also formed by controlled addition of pyrophosphoryl chloride to a stirred excess of dry liquid ammonia.[482–4] Rapid addition, however, gave approximately 70% conversion to a water-soluble amorphous polymer which on isolation had the empirical formula $P_2O_3N_3H_5$ or $P_2O_3N_4H_8$ dependent upon whether the soluble chloride was extracted with ice-water or liquid ammonia. The configuration



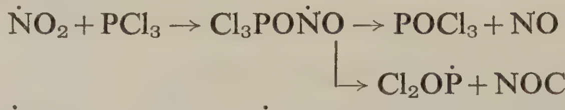
$$\left[ -\overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-O-\overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-NH- \right]_x$$

is proposed for the former compound.[481]

Addition compounds with pyrophosphoryl chloride as donor molecule, viz.: $2SbCl_5,P_2O_3Cl_4$ and $SnCl_4,P_2O_3Cl_4$, have been obtained and their infra-red spectra recorded.[485]

## 'TETRAPHOSPHORYL DECACHLORIDE'

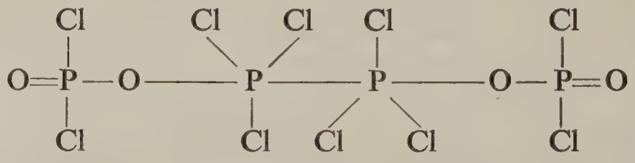
A colourless hygroscopic liquid: b.p. (1 mm. Hg) 105°C., f.p. 37°C., $d_4^{40}$ 2·017, mol. wt. (in camphene) 564, said to be tetraphosphoryl decachloride, $P_4O_4Cl_{10}$, was obtained[138, 486] in 6% yield by fractionation of the products of reaction between liquid dinitrogen tetroxide and phosphorus(III) chloride at −10°C. A free radicle mechanism was proposed:



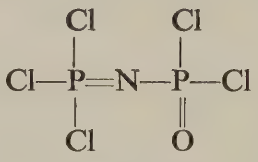
$$\dot{N}O_2 + PCl_3 \rightarrow Cl_3PO\dot{N}O \rightarrow POCl_3 + N\dot{O}$$
$$\hookrightarrow Cl_2O\dot{P} + NOCl$$

$$\dot{P}OCl_2 + POCl_3 \rightarrow \dot{P}_2O_2Cl_5\ (\equiv \tfrac{1}{2}P_4O_4Cl_{10})$$

The crystalline form was colourless, hygroscopic, soluble in organic solvents and gave slightly conducting solutions in thionyl chloride and nitrobenzene, while the formation of a hexachlorotin salt in carbon tetrachloride solution, formulated $(P_4O_4Cl_8)SnCl_6$, was taken[486] as indicating that two chlorine atoms per molecule were appreciably ionic in character. Reaction with water or organic amides was vigorous; the principal hydrolysis products were identified by paper electrophoresis as orthophosphate and hypodiphosphate, said[486] to indicate the presence of both 4 and 5 oxidation-state phosphorus atoms in the original compound. From a comparative study[487] of the infra-red and Raman spectra for phosphoryl chloride, pyrophosphoryl chloride, "$P_4O_4Cl_{10}$" and its phenyl ester, $P_2O_2(OPh)_5$,[488] it was concluded that 'tetraphosphoryl decachloride' was a chain molecule, symmetrically oriented about a direct P–P linkage thus:



and neither resonance[138] nor ring[489] stabilized as previously suggested. More recently[490] the structure of the compound has been identified as:



$$Cl_3P{=}N{-}P(O)Cl_2$$

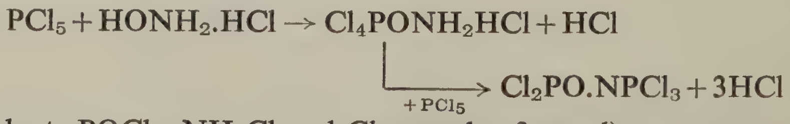
in agreement with the results of complete chemical analysis, and a nuclear magnetic resonance spectrum indicative of two 4-coordinated phosphorus atoms, each bonded in a different manner.

The compound (m.p. 35·7°, b.p. 102°/1 mm., $n_D^{38}$ 1·5256) isolated as above from the reaction between phosphorus trichloride and dinitrogen tetroxide was found[490]to be identical with those prepared from the reactions between phosphorus(V) chloride and:

(i) amidophosphoric acids in tetrachloroethane at 80°C.,[228] e.g.

$$3PCl_5 + H_2N.PO(OH)_2 \rightarrow 2POCl_3 + 4HCl + Cl_3PNPOCl_2$$

(ii) hydroxylamine hydrochloride in tetrachloroethane on heating up to 100°C.,[230] probably by:



$$PCl_5 + HONH_2.HCl \rightarrow Cl_4PONH_2HCl + HCl$$
$$\xrightarrow[+PCl_5]{} Cl_2PO.NPCl_3 + 3HCl$$

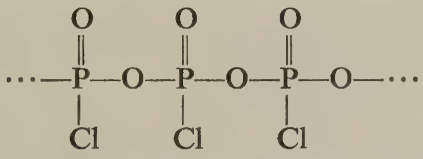
(side products $POCl_3$, $NH_4Cl$ and $Cl_2$ are also formed).

**Refs. p. 508**

(iii) ammonium chloride in nitrobenzene at 40° to 60°C. followed by reaction with sulphur dioxide, when $P_3NCl_{12}$ first formed (believed to be $[Cl_3P{:}NPCl_3^+][PCl_6^-]$) decomposes to $POCl_3 + Cl_3P{:}NPOCl_2$.[491]

## POLYPHOSPHORYL AND CYCLIC PHOSPHORYL CHLORIDES

The sealed tube reaction at 200° to 230°C. between phosphoryl chloride–phosphorus pentoxide mixtures with Cl:P atom ratio between 1·24 and 3 gives viscous single-phase liquids which can be fractionated (12 mm. Hg) to give phosphoryl chloride (b.p. 29°C.), pyrophosphoryl chloride (b.p. 90°C.) and a glassy residue of composition $PO_2Cl$.[471, 360] The latter, thought[471] on paper chromatographic evidence to contain cyclic trimetaphosphoryl chloride and linear polyphosphoryl chlorides of general formula $P_nO_{2n-1}Cl_{n+2}$, where $n = 4$ to 6, was said to lose pyrophosphoryl and trimetaphosphoryl chlorides on more prolonged distillation up to 130°C. (12 mm. Hg), and to leave a solid residue containing cross-linked phosphoryl chlorides. A compound of similar composition has been obtained by the action of dinitrogen tetroxide on phosphorus(III) chloride,[548] and in purer form by the action of dichlorine monoxide on trimeric phosphonitrilic chloride.[549] It is a colourless plastic solid, insoluble in the normal organic solvents. Very hygroscopic, it reacts violently with water giving hydrogen chloride and metaphosphoric acid. Its infra-red spectrum shows broad absorptions characteristic of a polymeric structure[549] such as:



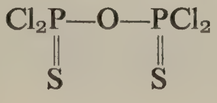
$$\cdots-\underset{\displaystyle Cl}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{\displaystyle Cl}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{\displaystyle Cl}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-O-\cdots$$

Nuclear magnetic resonance examination coupled with high vacuum distillation and thermal diffusion techniques have permitted analysis of the system $POCl_3$–$P_2O_5$ *in situ*[360] without the necessity for withdrawal of samples or of an intermediate hydrolysis step. The nuclear magnetic resonance spectra showed four peaks only, which were assigned to $POCl_3$ 'isolated', $POCl_2.O_{1/2}$ 'end', $O_{1/2}POCl.O_{1/2}$ 'middle' and $O_{1/2}PO.O_{1/2}.O_{1/2}$ 'branched' structural units; and for the equilibrium defined by the two equations:

$$POCl_2.O_{1/2} + O_{1/2}PO.O_{1/2}.O_{1/2} \rightleftharpoons 2O_{1/2}POCl.O_{1/2}$$
$$POCl_3 + O_{1/2}POCl.O_{1/2} \rightleftharpoons 2POCl_2.O_{1/2}$$

values of the equilibrium constants were found to be 0·42 and 0·64, respectively. These are considered to be reasonably close to 0·33, the theoretical value for ideally random reorganization. Thus, chlorine and bridging oxygen atoms were considered to exchange sites on the phosphorus atom in an approximately random manner. At Cl:P atom ratio = 2:1, 12% of the total phosphorus at equilibrium was present as pyrophosphoryl chloride, cf. 15% calculated for ideally random reorganization. The phosphoryl and pyrophosphoryl chlorides may be fractionated at room temperature (1 and $10^{-4}$ mm. Hg, respectively) without further reorganization of the mixture; above 65°C., however, appreciable further reorganization occurs during the distillation.[360]

In a similar series of experiments, phosphoryl chloride–phosphorus pentoxide–thiophosphoryl chloride–phosphorus pentasulphide mixtures with atom ratio Cl:P from 1·5 to 2 gave homogeneous liquid products only when the atom ratio S:P was unity. Such products were mainly mixed thionophosphoryl chlorides, i.e. with sulphur replacing the non-bridging oxygen atom. High vacuum distillation again gave phosphoryl and pyrophosphoryl chloride fractions, while some thionopyrophosphoryl chloride,



$$Cl_2\underset{\displaystyle S}{\underset{\|}{P}}-O-\underset{\displaystyle S}{\underset{\|}{P}}Cl_2$$

separated at $10^{-5}$ mm. over the temperature range 0° to 35°C. At higher temperatures appreciable further reorganization occurred.[360]

Dichlorophosphoric acid, $d_4^{25}$ 1·6878, m.p. $-28$°C.,[475] is miscible with water at room temperature, undergoing gentle hydrolysis to phosphoric and hydrochloric acids.[361] Addition to phosphoryl, thionyl, sulphuryl or trimethylsilane chloride followed by rapid distillation gave[474] dichlorophosphoric anhydrides thus:

$$\begin{array}{lll} & & \text{Yield} \\ HPO_2Cl_2 + POCl_3 & = OPCl_2.OPOCl_2 + HCl & 35\% \\ HPO_2Cl_2 + SOCl_2 & = OPCl_2.OSOCl + HCl & \multirow{2}{*}{\Big\}\ 15 \text{ to } 19\%} \\ HPO_2Cl_2 + SO_2Cl_2 & = OPCl_2.OSO_2Cl + HCl & \\ HPO_2Cl_2 + Me_3SiCl & = OPCl_2.OSiMe_3 + HCl & 90\% \end{array}$$

The pyrolysis products of dichlorophosphoric acid have been variously identified as pyrophosphoryl chloride and trimetaphosphoryl chloride at 100°C.,[475] phosphoryl and pyrophosphoryl chlorides and condensed phosphoric acids at 100° to 380°C.,[98] and as hydrochloric and condensed phosphoric acids.[361] It was shown[360] that the characterization of polyphosphoryl chloride mixtures by chromatographic methods involves major errors arising from possible degradation and condensation reactions inherent in the hydrolysis step. A wider application of nuclear magnetic resonance techniques must lead to a better understanding in this field.

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## SECTION XV

# PHOSPHORUS BROMIDES

BY R. H. TOMLINSON

## PHOSPHORUS TRIBROMIDE

### Preparation

Reaction between liquid bromine and white phosphorus is vigorous and in practice is moderated by carrying it out in phosphorus(III) bromide as solvent.[1] On the laboratory scale, independent investigators[2–3] commend a similar process, adding dropwise not more than 75% of the theoretical quantity of bromine to dried red phosphorus contained in refluxing phosphorus(III) bromide, thereby minimizing both the vigour of the reaction and the formation of phosphorus(V) bromide. Distillation gives 94% yields based on the bromine. A similar procedure giving phosphorus(III) bromide of high quality has been described more recently.[83] Other diluents, e.g. benzene, may be used, and provide similar yields[4] after separative distillation. Tagged phosphorus tribromide was obtained[5] by bromine exchange, on shaking phosphorus(III) bromide with excess of neutron-irradiated ethyl bromide at room temperatures and separating on the steam bath. Exchange of bromine in phosphorus tribromide with tagged bromine in carbon tetrachloride solution at 20°C. is also rapid, and presumably occurs by intermediate formation of pentabromide.[6]

### Physical Properties

The density, $d_4^t$, from 0° to 158°C. is given[7] by:

$$2{\cdot}9231 - 2{\cdot}458\,.\,10^{-4}t + 3{\cdot}78\,.\,10^{-7}t^2 - 2{\cdot}81\,.\,10^{-9}t^3$$

Extrapolation from density measurements at −79°C. gave[8] the molar volume at 0°K. = 76·1 ml. Vapour pressure and related data are:

| Range °C. | $\log_{10} p_{(\text{mm.})}$ | b.p. °C. | Latent heat of vaporization at the b.p. (kcal.) | Ref. |
|---|---|---|---|---|
| 40–173 | $7{\cdot}6787 - 2137{\cdot}9/T$ | 172·8 | 9·77 | 9 |
| 70–185 | $7{\cdot}498 - 2061/T$ | 173·3 | 9·42 | 10 |

The heat of hydrolysis ($\Delta H_{\text{obs.}}$) for the reaction: $PBr_3 + 3H_2O = H_3PO_3 + 3HBr$ is $-67{\cdot}2 \pm 0{\cdot}6$ kcal./mole, from which the value $-46{\cdot}5$ kcal./mole was obtained[11] for the heat of formation ($\Delta H^\circ_{f_{25}}$) of phosphorus(III) bromide from its elements. A value of $-41{\cdot}6$ kcal./mole is based[12] on the best data for phosphorus(III) chloride (see Section XIV, page 466) and the derived value therefrom (viz., $-227{\cdot}1$ kcal./mole) for the heat of formation of phosphorous acid. Values of standard heat ($\Delta H^\circ_f$), free energy ($\Delta F^\circ_f$) and equilibrium constant ($\log K_f$) of formation for phosphorus(III) bromide vapour at 25°C. are given[13–5] as: $-35{\cdot}9$, $-41{\cdot}2$ (in kcal./mole) and 30·19, respectively. Later values of the standard enthalpy of formation of phosphorus(III) bromide vapour, liquid, and crystalline solid at 298°K. have been given as $\Delta H^\circ_f(\text{g}) = -30{\cdot}7$, $\Delta H^\circ_f(\text{l}) = -41{\cdot}7$, and $\Delta H^\circ_f(\text{c}) = -45{\cdot}2$ kcal./mole, respectively.[90] Enthalpy, free energy and standard entropy functions for the vapour state between

298·1° and 800°K. have been derived[14, 16]; and a selection of the data is given in Table I.

*Table I.—Thermodynamic Properties of Phosphorus(III) Bromide*[14]

| Temperature °K. | $-\frac{G^\circ - H^\circ}{T}$ g.-cal./mole/deg. | $H^\circ - H^\circ_0$ g.-cal./mole | $S^\circ$ g.-cal./mole/deg. |
|---|---|---|---|
| 298·1 | 68·89 | 4,250 | 83·15 |
| 350 | 71·28 | 5,210 | 86·17 |
| 400 | 73·31 | 6,160 | 88·71 |
| 500 | 76·82 | 8,060 | 92·94 |
| 600 | 79·72 | 9,980 | 96·35 |
| 700 | 82·32 | 11,930 | 99·36 |
| 800 | 84·64 | 13,890 | 102·00 |

Heat capacities in the vapour state over the same temperature range are expressed[17] by $C^\circ_p = 18{\cdot}154 + 0{\cdot}002045T - 15300/T^2$.

Dipole moment values, 0·61[18] and 0·52,[19] were derived from dielectric constant measurements in carbon tetrachloride or benzene solution. The viscosity from −15° to +60°C. is given by $\eta_{(\text{poise})} = c/(\nu - \omega)$, where $c = 0{\cdot}000521$ and $\omega = 0{\cdot}3205$.[20–1] Ultrasonic measurements[22] have provided the data given in Table III, Section XIV, page 469. The molar susceptibility of phosphorus(III) bromide is $89{\cdot}3 \times 10^{-6}$ e.m.u. and that of phosphoryl bromide $93{\cdot}9 \times 10^{-6}$ e.m.u. The exaltation due to the phosphoryl group is almost exactly that found for the corresponding chlorides.[84]

Raman spectra measurements have shown reorganization in phosphorus(III) halide mixtures $PBr_3$–$PCl_3$[23] and $PBr_3$–$PI_3$[24] at room temperature with formation of mixed phosphorus(III) bromohalides. The micro-wave spectrum for phosphorus(III) bromide is recorded[25]; the far infra-red absorption spectrum was measured,[26] vibrational fundamentals being assigned and force constants calculated. The $^{31}P$ nuclear magnetic resonance spectrum of phosphorus(III) bromide[85] compared with that in a series of other halides and pseudohalides shows that Br is less electronegative than Cl, NCO or NCS (see also Section XIV, page 468).

## Chemical Properties

The aqueous hydrolysates of phosphorus(III) bromide showed strongest absorption in the ultra-violet–visible range when the hydrolysis had been freshly carried out under controlled conditions at pH 5·7 and 0°C.[27–8] The absorption was thought[27] to indicate maximum yield of an unstable "α-form" of phosphorous acid, $P(OH)_3$. Paper chromatographic analysis of the hydrolysate following dissolution of phosphorus(III) bromide in sodium bicarbonate suspension at 0°C. showed[29] the presence of orthophosphate and phosphite, trisodium diphosphite, hypophosphate and isohypophosphate, and also an unidentified product believed to contain P–O–P and P–P bonds; some phosphine is also formed. Similar products are obtained from the hydrolysis of phosphorus(III) bromide in cold aqueous sodium hydroxide[86] (see also Section XIV, page 471). The reaction of phosphorus(III) bromide with phosphorous acid is reversible, and because of the solubility of hydrogen bromide in the reaction medium lower yields of pyrophosphorous acid are obtained than in the analogous reaction of phosphorus(III) chloride.[87]

If phosphorus tribromide is caused to react under reflux with potassium chlorate, oxidation to phosphoryl bromide proceeds to 80% in 3 hr.[30] Oxidation in the vapour phase is catalyzed by dinitrogen tetroxide (not by $NO_2$ or NO) over a limited range of temperatures and oxygen pressures. The velocity constants up to 100°C. are proportional to the partial pressure of $N_2O_4$; outside defined limits the reaction is explosive, and the products include phosphorus pentoxide and bromine[31] (cf. Mellor, VIII, 1032).

**Refs. p. 525**

In the vapour phase with hydrogen under electrodeless discharge some reduction to phosphorous acid and an unidentified liquid impurity occurred.[32] Dropwise addition of phosphorus(III) bromide to powdered magnesium in refluxing absolute ether is said[33] to give red phosphorus of 99% purity. Reduction also occurs at temperatures between −115° and 0°C. with lithium hydride, aluminium hydride, or lithium aluminium hydride in dry ether[34]; the products are phosphine and a yellow solid of composition $(PH)_x$, the relative proportions of which vary with the temperature and reductant used.

Thermal analysis provides no evidence of compound formation in $PX_3$–iodine systems (where X is chlorine or bromine) and the electrical conductivity of each system is lower than that of molten iodine.[35] Addition of $PX_3$ to iodine chloride is exothermic; the systems show eutectics at 10 mole-% $PCl_3$ and 33 mole-% $PBr_3$, respectively, have high specific conductances (up to $4 \times 10^{-2}$ mho cm.$^{-1}$) and give rise to compounds of composition $PX_6I$, identical with those precipitated from saturated solutions of $PX_5$ with IX in carbon disulphide or carbon tetrachloride,[36] or isolatable from the $PX_5$–iodine[37] or $PX_5$–iodine chloride[38] systems. The reaction: $PX_3 + 2\,IX = PX_5 + I_2$ therefore, is thought to be reversible, complex formation with $PX_5$ occurring in the presence of IX. The high electrical conductance of these systems is explained on the basis of ion formation according to $PX_6I \rightleftharpoons [PX_4]^+ + [IX_2]^-$, while a more general study of ionization in molten iodine bromide[39] (specific conductance at 55°C. $= 7 \times 10^{-6}$ mho cm.$^{-1}$) showed $PBr_6I$ to be solvo-basic in that solvent. The maximum in the thermal diagram for the phosphorus(V) bromide–iodine system (Fig. 1) is attributed[37] to formation of $PBr_6I$ according to the scheme outlined above. The overall equation may be written: $3PBr_5 + I_2 = PBr_3 + 2PBr_6I$. A spectrophotometric study in the 300 to 600 mμ region confirms[40] the dissociation of $PX_6I$ solutions in polar and non-polar solvents as ionic and molecular, respectively:

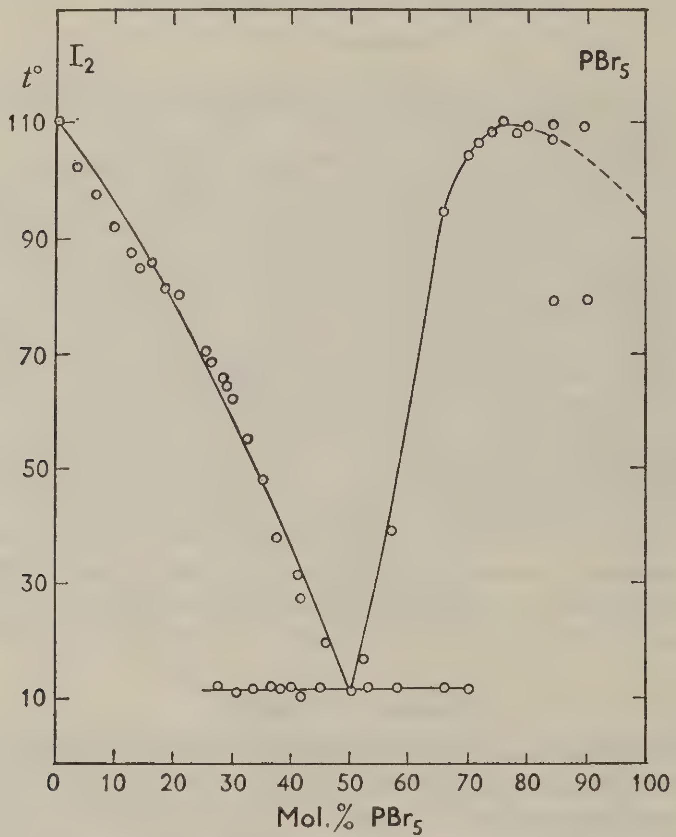

FIG. 1.—Thermal analysis of the system $PBr_5$–$I_2$

$$PX_4^+ + IX_2^- \underset{\text{in MeCN}}{\rightleftharpoons} PX_6I \underset{\text{in } CCl_4,\ C_2H_4Cl_2 \text{ or } CS_2}{\rightleftharpoons} PX_5 + IX$$

Refs. p. 525

While phosphorus(V) chloride shows no tendency towards further dissociation in non-polar solvents, phosphorus(V) bromide undergoes approximately 50% dissociation according to $PBr_5 \rightleftharpoons PBr_3 + Br_2$, the dissociation constants in carbon tetrachloride or ethylene dichloride solution being[41] of the order 2 to $3 \times 10^{-3}$. The compound $PBr_5,2CCl_4$ slowly hydrolyzes in moist air, has no sharp m.p., decomposes at 86°C. and forms as an orange-yellow precipitate on mixing equimolar carbon tetrachloride solutions of phosphorus(III) bromide and bromine,[40] or deposits from saturated phosphorus(V) bromide solutions in carbon tetrachloride.[42] The compound $2PCl_5,CCl_4$ is similarly obtained[42] from phosphorus(V) chloride solutions in carbon tetrachloride. Addition of phosphorus(III) bromide to phosphorus(V) chloride gives liquid phosphorus(III) chloride and red crystals of composition $PCl_3Br_4$; with more phosphorus(III) bromide, yellow crystals of composition $PClBr_4$ are formed.[43] The relative electrical conductances of $PBr_5$, $PClBr_4$ and $PCl_3Br_4$ in nitrobenzene solution are respectively[43] 1:1·5:10. Fluorination of phosphorus(III) bromide occurs in the gas phase with calcium fluoride at 140°C. or with powdered antimony(III) fluoride and bromine as catalyst at 70° to 170°C.; the products are phosphorus(III) fluoride and mixed fluorobromides.[44–5]

A cryoscopic and ebullioscopic investigation of mutual solutions of the halides of the elements belonging to the 4th and 5th groups of the Periodic Table[46] has indicated ready halogen exchange between the titanium and tin tetra-, and phosphorus, arsenic and antimony trihalides; well crystallized complexes of composition $TiCl_4,PCl_3$ and $TiBr_4,2PBr_3$ were also isolated. Fusion curves for each of the systems $PBr_3$–$SbBr_3$, $PBr_5$–$S_2Br_2$ and $PCl_3$–$SnCl_4$ show one branch only, whilst those for $PBr_3$–$SnBr_4$ and $PBr_5$–$AsBr_3$ show eutectics at −50°C. (84 mole-% $PBr_3$) and 23·5°C. (17·5 mole-% $PBr_5$) respectively; the curve for the system $PBr_3$–$AsBr_3$ shows a continuous series of solid solutions.[47–8] Phosphorus(III) and (V) bromides are readily soluble in molten antimony tribromide giving red solutions.[49]

Addition of gaseous trimethylamine to liquid phosphorus(III) bromide at 0°C. gives[50] crystals of the 1:1 complex for which the heat of dissociation (calculated from vapour pressure measurements at 0° to 28°C.) is 19·9 kcal./mole. The heat of solution ($Me_3N$ gas in $PBr_3$ liq.) is −9·5 kcal./mole, which together with the latent heat of vaporization $Me_3N$(l.), viz., 6·4 kcal./mole, provides an estimated P–N bond energy of 3·1 kcal.; the value 6·4 kcal. was obtained for the P–N bond in the corresponding phosphorus(III) chloride complex $Me_3N,PCl_3$ (Section XIV, page 475). Such complexes may be examples of triply connected phosphorus behaving as an electron pair acceptor in $\sigma$-bond formation.[50] Formation of a boron tribromide complex $PBr_3,BBr_3$ (cf. Mellor, VIII, 1033) was confirmed[51]; the product, m.p. 61° to 62°C., remains unchanged *in vacuo* at room temperature. It is also formed by the action of excess of boron(III) bromide on diphosphorus tetrachloride[88] or by the interaction of boron(III) bromide and phosphorus(III) bromide in carbon disulphide at −40°.[89] The yellow compound $PBr_3,BI_3$, m.p. 50° (decomp.), has been prepared similarly,[89–90] and thermodynamic data for these and allied compounds given as follows (units kcal./mole)[90]:

| Compound | $PI_3,BI_3$ | $PI_3,BBr_3$ | $PBr_3,BI_3$ | $PBr_3,BBr_3$ |
|---|---|---|---|---|
| $\Delta H^{\circ\,(a)}$ | −21·8 | −69·9 | −37·8 | −15·2 |
| $\Delta H_1{}^{(a)}$ | −55·8 | −96·6 | −64·3 | −34·4 |
| $\Delta H(c \rightarrow g)^{(b)}$ | 34·0 | 31·3 | 30·0 | 27·3 |
| $D(P–B)^{(c)}$ | 21·8 | 65·3 | 34·3 | 7·1 |

(a) Enthalpy change of the reactions
$PX_3(\text{standard state}) + BY_3(\text{standard state}) \rightarrow PX_3,BY_3\ (c)$ $\Delta H^\circ$
$PX_3(g) + BY_3(g) \rightarrow PX_3,BY_3\ (c)$ $\Delta H_1$
(b) Enthalpy of sublimation.
(c) P–B bond dissociation energy.

A vigorous exothermic reaction occurs between ruthenium tetroxide and phosphorus(III) bromide in carbon tetrachloride solution; distillation *in vacuo* of the phosphoryl bromide from the product left a black residue thought[52] to be a mixture of $RuO_2$ and $RuO_2,PBr_3$.

Phosphonitrilic bromides (which are unstable in air, and hydrolyzed by boiling water, soften at 23° to 40°C. and give elastomeric solids at 195°C. *in vacuo*) are obtained by causing phosphorus(III) bromide to react (i) with sodium azide at 162° to 167°C.[53] according to:

$$PBr_3 + NaN_3 \rightarrow (Br_2PN)_n + N_2 + NaBr$$

or (ii) with ammonium bromide + bromine in *sym.*tetrachloroethane at 110° to 150°C. over 7 days.[54] The latter reaction, starting from differing phosphorus halide–ammonium halide–bromine mixtures, leads[55] to phosphonitrilic bromochlorides, viz.:

| | | |
|---|---|---|
| $P_3N_3Cl_5Br$ | m.p. | 122·5° to 123·5°C. |
| $P_3N_3Cl_4Br_2$ | ,, | 134·5° to 136·5°C. |
| $P_3N_3Cl_2Br_4$ | ,, | 165·5° to 167·0°C. |

and, by stopping the reaction at 110° to 120°C., the addition compound $PNBr_2,PBr_5$ is obtained.[54]

Tetrakistribromophosphine nickel, $Ni(PBr_3)_4$, forms as small, pale-yellow thermochromic crystals (deep orange at room temperature) on treating $Ni(PCl_3)_4$ with excess of phosphorus(III) bromide at 70°C., removing phosphorus(III) chloride *in vacuo* and cooling to $-38$°C.[56]

Polymerization of white to red phosphorus in the presence of phosphorus(III) chloride or bromide or iodine as catalyst gives a product containing halogen, variously considered to be incorporated as a mixed polymer,[57] or as terminal atoms in the general polymeric structure.[58] A similar yellow amorphous involatile polymeric product of the empirical formula $P_2BBr_3$ is obtained by reaction of boron(III) bromide with white phosphorus in chloroform.[91]

Comparative solubilities (g./100 g.) of various phosphorus halides in liquid sulphur dioxide under pressure[59] may be summarized thus:

| | $POCl_3$ | $PCl_3$ | $PBr_3$ | $PI_3$ |
|---|---|---|---|---|
| 0°C. | miscible in all proportions | | 12 | — |
| 25°C. | ,, | ,, | 20 | 0·3 |

However, phosphorus(III) bromide and *iso*thiocyanate have been shown to react with liquid sulphur dioxide, slowly at the boiling point and quite rapidly at 50° under pressure, according to the equation:

$$3PX_3 + SO_2 \rightarrow PSX_3 + 2POX_3$$ [92]

Formation of the compound $PBr_3,3C_6H_5CHO$ in the phosphorus(III) bromide–benzaldehyde system is indicated[60] by the shape of the density, viscosity and surface tension isotherms at 30° and 50°C. Phosphorus(III) bromide, unlike phosphorus(III) chloride, reacts with tetraethyl silicate giving ethyl bromide and a polymer containing phosphorus, oxygen and silicon.[93]

## PHOSPHORUS PENTABROMIDE

The preparation of phosphorus(V) bromide by slow addition of bromine to yellow phosphorus in carbon disulphide solution, initially a violent reaction, is described.[61] Purification is effected by recrystallization from nitrobenzene and washing with absolute ether, the last traces of which are removed in a stream of nitrogen. The substance may also be conveniently prepared by reaction of equimolecular quantities of phosphorus(III) bromide and bromine at 30–35°C. in an anhydrous inert solvent, such as a lower aliphatic polyhalide, in which the product is insoluble.[94]

**Refs. p. 525**

## Physical Properties

From exchange studies with labelled chlorine or bromine in carbon tetrachloride solution,[62–3] it has been concluded that all the five halogen atoms in phosphorus(V) chloride or bromide are equally reactive. Later (see Section XIV) it was shown[64–5] that the three equatorial chlorine atoms of $PCl_5$ exchange much more rapidly with tagged chlorine than do the two apical chlorine atoms. Absorption spectra in the 300 to 600 m$\mu$ region for solutions of phosphorus(V) bromide in non-polar solvents, although closely similar to those of bromine solutions, were shown[41] to be due in large part to undissociated $PBr_3,Br_2$, the degree of dissociation being about 50%. Conductivity and transport experiments with solutions of phosphorus(V) bromide in acetonitrile have confirmed the presence of $PBr_4^+$ and $PBr_6^-$ ions, while conductimetric titration of phosphorus(III) bromide in the same solvent with bromine gives a break at the 1:1 mole ratio only.[66] In contrast with acetonitrile, nitrobenzene solutions of phosphorus(V) bromide have low conductivity:

| solvent | acetonitrile | | | | nitrobenzene |
|---|---|---|---|---|---|
| moles $PBr_5$/l. | 0·0152 | 0·0195 | 0·0296 | 0·0729 | 0·147 |
| molar conductance (mho cm.$^2$ mole$^{-1}$) | 13·95 | 14·25 | 12·26 | 7·86 | 0·224 |

Cryoscopic data for the $PBr_3$–$Br_2$ system in nitrobenzene were interpreted[66] in terms of two equilibria involving $PBr_5$ and to a lesser extent $PBr_7$ species. There appeared to be about 90% dissociation, and the structure of the entities was not decided. The crystal structure of phosphorus(V) bromide differs completely from that of phosphorus(V) chloride (Section XIV, page 477) being orthorhombic with $a$, $b$ and $c = 5{\cdot}62 \pm 0{\cdot}03$, $16{\cdot}91 \pm 0{\cdot}03$ and $8{\cdot}29 \pm 0{\cdot}03$ A., respectively.[67] There are 4 molecules per unit cell, the space group is $D_{2h}^{11}$–$Pbcm$ with all the phosphorus atoms crystallographically and chemically equivalent. The structure consists of tetrahedral $[PBr_4]^+$ groups together with $Br^-$ ions; the P–Br bond length is 2·2 A. and the shortest P to $Br^-$ distance = 4·3 A. A Raman investigation[68] confirms the ionic structure and gives force constants (Urey–Bradley field) $K_1 = 2{\cdot}19$, $K_2 = 0{\cdot}18$ and $\gamma_3 = 0{\cdot}028$, each $\times 10^5$ dynes/cm.

Vapour pressure measurements[61] between 75° and 83·5°C. are expressed within ±1% by $\log_{10} p_{\text{mm.}} = 10{\cdot}7867 – 3020{\cdot}3/T$. At higher temperatures the plot of $T \log_{10} p$ versus $t$°C. was curved and cut the lower straight line portion at 83·8°C., which is thought to be the maximum sublimation temperature of dissociating phosphorus(V) bromide. At this temperature the originally 2-phase system becomes 3-phase with the appearance of the liquid form of phosphorus(III) bromide. Vapour pressure measurements over the temperature range 32·5° to 75°C.[69] are expressed by $\log_{10} p_{(\text{mm.})} = 10{\cdot}1713 – 2895{\cdot}7/T$. The observed vapour density[69] is constant from 65° to 180°C. and corresponds to a molecular weight one-half that of phosphorus(V) bromide. Thus the equilibrium is of the type: solid ⇌ gas + gas. Writing the total pressure as $P_{(\text{atmospheres})}$, the equilibrium constant $K_p$ becomes $P^2/4$ and $\log_{10} K_p = 13{\cdot}979 – 5791{\cdot}4/T$. The heat of the dissociation: $PBr_5(s) \rightleftharpoons PBr_3(g) + Br_2(g)$ is therefore 26·5 kcal./mole. From the heat of hydrolysis of phosphorus(V) bromide a value of $\Delta H_f^\circ = -54{\cdot}6 \pm 1{\cdot}2$ kcal./mole has been deduced for the standard enthalpy of formation of crystalline $PBr_5$ at 298°K.[95]

## Chemical Properties

Slow addition of arsenic(III) fluoride to a stirred suspension of phosphorus(V) bromide in carbon tetrachloride or disulphide at 30° to 50°C. gives white tetrabromophosphonium hexafluorophosphate, $[PBr_4][PF_6]$[70] (see Section XIII, page 454).

Addition of iodine chloride to phosphorus(V) bromide in carbon tetrachloride solution gives red needle crystals of composition $PBr_5,ICl$, m.p. 112·5°C. and stable on storage in a sealed tube.[71] Solutions in benzene or carbon tetrachloride are non-conducting and cryoscopic values agree with the theoretical molecular weight.

Electrical conductance in nitrobenzene is greater than that of an equimolar solution in iodine chloride; the formulation: $[PBr_4][BrICl]$ is suggested.

On heating phosphorus(V) bromide with dihydroxydifluoroboric acid the following reaction occurs[72]:

$$3H_3BO_2F_2+3PBr_5 = BPO_4+2POBr_3+2BF_3+9HBr$$

Phosphorus(V) bromide–chloride mixtures or phosphorus(V) bromochlorides react with acetic acid, alcohols or acetone to give phosphoryl chlorobromides.[73] The reaction between phosphorus(V) bromide and acetic acid:

$$CH_3COOH+PBr_5 \rightarrow POBr_3+HBr+CH_3COBr$$

(more conveniently in *tert.*-butanol or dry *iso*propanol–ether) gives 85% yields of phosphoryl bromide on distillation.[74] The reaction between acetic anhydride and phosphorus(V) chloride:

$$(CH_3CO)_2O+PCl_5 \rightarrow 2CH_3COCl+POCl_3$$

has been recently noted.[75]

## PHOSPHORUS POLYBROMIDES

Thermal analysis of the phosphorus–bromine system[76] shows the existence of two polybromides of composition $PBr_7$ and $PBr_{17}$ besides the normal phosphorus(III)and (V) bromides. The heptabromide is obtained as red crystals, decomposing into two liquid layers at 106·5°C.; the polybromide $PBr_{17}$ melted at 14·5°C. The former compound was thought to arise from disproportionation of the pentabromide at 99°C. according to:

$$2PBr_5 \rightleftharpoons PBr_3+PBr_7$$

## PHOSPHORYL BROMIDE

The preparation from phosphorus(III) bromide, bromine and phosphorus pentoxide has been described in detail[77]; the solid phosphorus(V) bromide first formed is mixed with phosphorus pentoxide in the mole ratio 3:1, gently heated until liquid, then more strongly, and finally distilled to give an 80% yield of phosphoryl bromide based on the phosphorus tribromide used. Redistillation at 12 mm. Hg and fractionation under high vacuum at 100° to 120°C. has yielded[78] pure phosphoryl bromide for determination of the atomic weight of phosphorus. (Hydrolysis in cold aqueous ammonia followed by precipitation with silver nitrate gave the value $30{\cdot}973 \pm 0{\cdot}003$.) Pure phosphoryl bromide, m.p. 56·4°C., has also been obtained[79] by repeated fractional freezing until the product is cryoscopically homogeneous. Bromination of phosphoryl chloride with gaseous hydrogen bromide proceeds to 99% in the presence of 0·5% of aluminium chloride or bromide as catalyst at 80°C.[80] Other formative methods to which earlier reference has been made include the reactions between: phosphorus(III) bromide vapour[31] or liquid[96] and oxygen with nitrogen tetroxide as catalyst, phosphorus(III) bromide liquid and potassium chlorate at 170° to 180°C.[30] (page 519) and phosphorus(V) bromide and acetic acid, acetone,[73] tertiary butanol in absolute ether[74] or difluoroboric acid[72] (page 524).

### Physical Properties

The molar volume at 0°K. = 82·8 c.c.[8] Vapour pressure measurements between 150° and 205°C.[81] are expressed within ±1% by $\log_{10}p_{(\mathrm{mm.})} = 7{\cdot}875 - 2323{\cdot}2/T$; b.p. = 192·0°C. and latent heat of vaporization = 10·9 kcal./mole. The heat of hydrolysis ($\varDelta H_{\mathrm{obs.}}$) for the reaction:

$$POBr_3(c)+(n+3)H_2O(l) \rightarrow H_3PO_4+3HBr \text{ in } nH_2O(l)$$

with solid phosphoryl bromide at 25°C. is −80·8 ± 0·5 kcal./mole, from which the derived values of standard heat of formation ($\Delta H^\circ_{f_{25}}$) for (c) and (g) phases were −110·1 and −95·1 kcal./mole, respectively[11]; the last figure incorporates an estimated heat of sublimation = 15 ± 1 kcal./mole. Densities from 62° to 130°C. are expressed by $d^t_4 = 2{\cdot}8335 - 0{\cdot}002487(t-55)$, surface tension from 55° to 100°C. by $\gamma = 41{\cdot}2 - 0{\cdot}167(t-55)$ dynes/cm. and free surface energy ($\gamma . V_M^{2/3}$ where $V_M$ is molar volume) by $\omega = 895 - 3{\cdot}22(t-55)$; the mean parachor is 255·3,[79] cf. 254·3.[82] The plot of log viscosity against $1/T$ is slightly curved, values at 54·5° and 93·1°C. being 2·729 and 1·655 centipoise, respectively; the activation energy of viscous flow decreases from 3·21 kcal./mole at the m.p. to 2·85 kcal./mole at 90°C.[79] The molar susceptibility of phosphoryl bromide has been determined[84] (see page 519). Infra-red and Raman spectroscopic data have also been recorded.[97]

### Chemical Properties

The specific conductance of phosphoryl bromide is $< 4 \times 10^{-8}$ mho cm.$^{-1}$ The fusion diagram for the gallium bromide–phosphoryl bromide system[79] establishes the formation of a 1:1 compound having m.p. 154°C.; it is, however, less stable than the analogous $GaCl_3,POCl_3$ complex. A comparison of the conductivity data at their respective melting points bears out the analogy.

| | $GaBr_3,POBr_3$ (m.p. 154°C.) | $GaCl_3,POCl_3$ (m.p. 118·5°C.) |
|---|---|---|
| Specific conductance (mho cm.$^{-1}$) | $1{\cdot}0 \times 10^{-3}$ | $1{\cdot}26 \times 10^{-3}$ |
| Molar conductance (mho cm.$^2$ mole$^{-1}$) | 0·21 | 0·227 |
| Reduced conductivity ($\mu . \eta$ mho cm.$^2$ centipoises) | 1·0 | 0·442 |

The Raman spectra for the molten gallium chloride–phosphoryl chloride complex indicates an ionic formula $POCl_2^+,GaCl_4^-$. At 161·2°C. the density of the gallium bromide–phosphoryl bromide complex was 2·875 g./c.c. and the viscosity 4·921 centipoises; the specific conductance increased from $1{\cdot}0 \times 10^{-3}$ mho cm.$^{-1}$ at zero time to a constant value of $2{\cdot}3 \times 10^{-3}$ mho cm.$^{-1}$ after 3 hr.[79]

Similar considerations support the existence of compounds of phosphoryl bromide with sulphur trioxide, tin(IV) bromide and chloride, aluminium(III) chloride, lithium bromide, and nitrogen bases such as quinoline, pyridine or dimethyl formamide.[98] The compounds $BCl_3,PBr_3$, $BBr_3,POBr_3$ (m.p. 150°C.), $AlCl_3,POBr_3$ (m.p. ca. 100° (decomp.)), $AlBr_3,POBr_3$ (m.p. 183°C. (decomp.))[99] and $TiOBr_2,2POBr_3$,[100] were identified in other investigations. Thermochemical studies[101] of the four compounds $POX_3,BY_3$ (X, Y = Cl or Br) have been reported in Section XIV, page 503.

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## SECTION XVI

# PHOSPHORUS IODIDES

BY R. H. TOMLINSON

## PHOSPHORUS DI-IODIDE

Phosphorus di-iodide (diphosphorus tetraiodide), $P_2I_4$, forms as unstable, red needle crystals, m.p. (heated quickly in a preheated bath) 125·5°C., from stoicheiometric mixtures of yellow phosphorus and iodine in carbon disulphide solution. The preparation originally described[1] (Mellor, VIII, 1038) has been modified[2] with respect to detail. The crystals[2] underwent considerable decomposition on storage, both in sealed ampoules and in stoppered flasks over calcium chloride. Preparation of phosphorus thioiodide, $P_4S_3I_2$, from its elements in carbon disulphide solution is described.[3] Its formation, from sulphur impurity in the carbon disulphide used, was considered[1] to account for the low m.p. reported for phosphorus di-iodide by earlier workers. *X*-Ray crystallography[4] shows the thioiodide to consist of two 5-member rings of 3 P and 2 S atoms joined by a common P–S–P linkage, the iodine atoms being bonded to the remaining P atom in each ring. A possible alternative explanation for impurities in phosphorus di-iodide is the disproportionation into phosphorus(III) iodide, which is discussed below.[15, 34]

Mixtures of solid iodine with red phosphorus, having atom ratios (I:P) between 1·33:1 and 3:1, undergo exothermic reaction on initiation by gentle heat. At the lower ratio, after stirring the reaction product for a further 1 hr. at 180° to 190°C. and taking up in chlorobenzene, a 40% yield of phosphorus di-iodide crystals (m.p. 126° to 127°C.) was obtained.[5] At the 3:1 ratio, crystallization of the reaction product from dichloroethylene gave dark-red phosphorus(III) iodide crystals (m.p. 60° to 61°C.) in 65% yield. Reaction between excess of red phosphorus and iodine or phosphorus(III) iodide in refluxing butyl iodide,[5] or between yellow phosphorus and phosphorus(III) iodide or methyl tetraiodophosphorane in carbon disulphide solution at room temperature, also results[6] in appreciable yields of the di-iodide. Phosphorus di-iodide with iodine also arises from the catalytic decomposition of phosphorus(III) iodide by ether.[35]

The reaction between yellow phosphorus and iodine in carbon disulphide has been reported to yield phosphorus di-iodide via several iodide intermediates, without breaking and reforming the P–P bond.[36] However, later workers have shown by $^{31}P$ nuclear magnetic resonance and ultra-violet spectrophotometry that there is an initial rapid reaction to form phosphorus(III) iodide which is followed by a slower reaction with excess of phosphorus, where present.[37]

### Physical Properties

Phosphorus di-iodide crystallizes in the triclinic system, its space group is $P\text{–}\bar{1}$ and there is one molecule per unit cell. The P–P and P–I distances are 2·21 (standard deviation 0·06) and 2·475 (standard deviation 0·028) A., respectively, with each phosphorus atom linked to two iodine atoms. The molecular symmetry is $2/m$, the two $PI_2$ groups being in the *trans* position to each other[7] as shown diagramatically in Fig. 1.

Ebullioscopy in carbon disulphide solution confirms the molecular formula $P_2I_4$. Dielectric constant measurements in the same solvent[8] gave values of 0·45 and

0·34 D. for the dipole moments of phosphorus di- and tri-iodides, respectively. A value of 0·24 D. was obtained for the dipole moment of the P–I bond; it was concluded[8] (in contrast to the *trans* configuration indicated above for the crystalline form) that the two $PI_2$ groups of the isolated molecule in solution are rotated about the P–P bond at an angle of approximately 85°. The infra-red spectrum of carbon disulphide solutions also appeared to support this staggered (*gauche*) configuration of $C_2$ symmetry for dissolved phosphorus di-iodide molecules.[38–9] However, it now seems probable that the compound in fact has the *trans* $I_2P{-}PI_2$ structure with $C_{2h}$ symmetry in both solid state and solution. This opinion is based on the absence of coincidences between the Raman and infra-red spectra, the similarity between the solid and solution spectra, and the fact that only two infra-red active and three Raman active fundamentals (two depolarized and one polarized) are observed.[40–1] Infra-red absorption bands seen at 303 and 328 cm.$^{-1}$ are assigned to phosphorus(III) iodide which, together with phosphorus, has been shown to arise by the dismutation of pure phosphorus di-iodide in carbon disulphide solution.[34] The presence of phosphorus(III) iodide, demonstrated by its $^{31}P$ nuclear magnetic resonance and ultraviolet spectra, may also account for the dipole moment observed by previous workers.[8] The $^{31}P$ nuclear magnetic resonance spectra for phosphorus di-iodide (in carbon disulphide solution) and for phosphorus tri-iodide (liquid) show chemical shifts, referred to aqueous phosphoric acid, of $-170 \pm 10$ and $-178 \pm 4$ p.p.m., respectively.[9] The density of the di-iodide at 20°C. is $4{\cdot}178 \pm 0{\cdot}002$ g./c.c.[8]

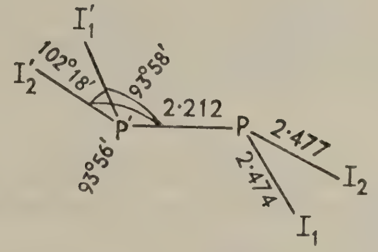

FIG. 1.—Molecular dimensions of $P_2I_4$. Non-bonded distances are, in A., $I_1I_2$, 3·856; $I_1P'$, 3·341; $I_2P'$, 3·434

## Chemical Properties

The products of hydrolysis of phosphorus di-iodide at 0°C. are hydrogen iodide, phosphine, hypophosphorous, phosphorous and phosphoric acids; while oxidation of the hydrolysate with hydrogen peroxide at an alkaline pH gave[10] up to 24% conversion into hypophosphoric acid ($H_4P_2O_6$). The presence of various P–P bonded phosphoric acids in the products of oxidative hydrolysis of either phosphorus di-iodide or of the lower phosphorus sulphides ($P_4S_3$, $P_4S_5$ or $P_4S_7$) has been reported.[11] In basic solution and the absence of oxidants the hydrolysis, like that of $P_2Cl_4$ (*q.v.*), appears to go according to the equations:

$$2P_2X_4 + 2H_2O \rightarrow P_2H_4 + P_2(OH)_4,$$
$$P_2(OH)_4 + H_2O \rightarrow H_3PO_2 + H_3PO_3$$

followed by:

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$ [42]

Phosphorus di-iodide solutions in carbon disulphide at 20°C. absorb 0·6 to 1 mole of oxygen per mole of $P_2I_4$ to give an amorphous yellow polymer, the reaction being approximately represented[12] by:

$$7P_2I_4 + 6O_2 \rightarrow 2/n(P_3I_2O_6)_n + 8PI_3$$

Refs. p. 532

With sulphur in boiling benzene or carbon disulphide solutions in the absence of daylight, the following reactions are reported[13]:

$$7P_2I_4+\tfrac{7}{4}S_8 = 2P_4S_7+6PI_3+5I_2$$
$$2P_2I_4+\tfrac{7}{8}S_8 = P_4S_7+4I_2$$

while from phosphorus tri-iodide with sulphur in carbon disulphide solution at 10° to 15°C., also in the absence of daylight, unstable thiophosphoryl iodide, $PSI_3$, has been crystallized.[14] The thioiodides: $P_4S_3I_2$, $P_2S_2I_4$ and $P_2SI_4$ (m.p., each with decomposition, 118°, 90° to 93° and 105° to 110°C., respectively), may be obtained by crystallization from carbon disulphide solutions of the elements in stoicheiometric proportions after standing in the dark for several days at room temperature.[3, 13] Crystals of the less stable thiophosphoryl iodide (m.p. 46° to 48°C. with decomposition) are obtained in a similar manner, but after 3 to 4 hr. standing at 10° to 15°C.[14] There is some evidence that an unstable complex, $P_2I_4,4S_8$, may be an intermediate in these reactions.[43]

In a study of various phosphorus halide–iodine systems,[15] it was shown that molten phosphorus di-iodide–iodine mixtures containing greater than 33 mole-% of phosphorus di-iodide gradually transform to phosphorus tri-iodide and iodine. The action of bromine on phosphorus di-iodide yields a mixture of the four halides $PBr_nI_{3-n}$ $(n=0-3)$.[44] Like other phosphorus halides, phosphorus di-iodide forms complexes, though these have been little studied. Thus it reacts with boron tribromide and tri-iodide (but not with the weaker Lewis acids $BF_3$ and $BCl_3$) and the unstable yellow complex $P_2I_4,2BBr_3$ has been isolated.[38] With aluminium(III) iodide three products are formed:

(1) A red amorphous solid, insoluble in carbon disulphide with an I:P ratio of approximately unity, and a P:Al ratio approximately 5:1.
(2) A small amount of the complex $2PI_3,AlI_3$.
(3) A major proportion of impure $P_2I_4,AlI_3$ (red-brown crystals, m.p. 122–5°C.).

Products (1) and (2) presumably arise from the partial disproportionation of $P_2I_4$ in the sense:

$$P_2I_4 \rightarrow (\text{–PI–})_n+PI_3$$ [45]

## PHOSPHORUS TRI-IODIDE

Phosphorus(III) iodide, m.p. 61°C., forms as hygroscopic, red tabular crystals from carbon disulphide solutions of iodine with an equivalent amount of yellow (or suspended red) phosphorus,[1, 37] or by recrystallization from dichloroethylene of the product of the exothermic reaction between stoicheiometric amounts of red phosphorus and solid iodine.[5] Its formation has also been noted in the reaction between phosphorus and iodine vapours at ordinary temperatures[16]; the position of the deposit of solid tri-iodide is dependent upon such factors as tube shape, total pressure and the admission or otherwise of hydrogen or wood charcoal. Other reactions by which it arises include the decomposition of $P_2I_4$ by heat,[34] iodine,[15] or bromine.[44]

### Properties

The complete Raman spectrum for phosphorus(III) iodide was obtained[17] using He 6678·2 A. radiation; the fundamental frequencies were assigned, and force constants: $K=1{\cdot}21$, $K'=0{\cdot}06$, $H=0{\cdot}18$ and $H'=0{\cdot}03$ dynes $\text{cm.}^{-1}\times 10^5$ evaluated, using an assumed pyramidal angle of 102°. Raman methods have also shown[18] the presence of mixed phosphorus(III) halides in mixtures of phosphorus(III) iodide and chloride, while Hg 4358 A. radiation in about 15 hr. produces change of the type: $PClI_2+PCl_3=2PCl_2I$ with loss of colour, the reaction being reversible on removal of the light source. Mixed bromoiodides have been demonstrated similarly.[44]

The enthalpy of formation of phosphorus(III) iodide was determined by aqueous hydrolysis.[46] The value obtained, $-10{\cdot}7$ kcal./mole, was in good agreement with previous values.[47]

Published values for the dipole moment of phosphorus tri-iodide (from observations in carbon disulphide solution) are 0·0[19] and 0·34 D.[8]

Hydrolysis at 0°C. in sodium bicarbonate buffered solutions gives phosphine and salts of a number of reduced acids (see Section XIV, page 471) as well as ortho- and pyrophosphates.[20] Sodium hydroxide hydrolysis yields similar results, though no phosphine can be detected.[48]

Conductivity and cryoscopic methods have indicated[21] that the association factor of phosphorus(III) iodide in molten iodine (at 111°C.) increases with increasing $PI_3$ concentration. Conductivity data for the system at 130° and 140°C.[22–3] plotted against concentration show a negative temperature coefficient, with maximum specific conductance $1{\cdot}24 \times 10^{-4}$ mho cm.$^{-1}$ at 9·7 mole-% $PI_3$. An electrolytic dissociation of associated iodide molecules of the type:

$$(MI)_n \rightleftharpoons (M_nI_{n-m})^{m+} + mI^-$$

rather than formation of polyiodide is suggested.[23] Specific gravity[24] and viscosity[25] changes for the system are reported, a maximum in the viscosity–composition curve coinciding[25] with the minimum in the specific gravity–composition curve.

Double decomposition reactions with elimination of the more volatile phosphorus(III) chloride occur on heating phosphorus(III) iodide with bismuth, lead, arsenic, antimony, tin, titanium[26] and germanium[27] chlorides; but no reaction was observed[28] with zirconium or thorium tetrachlorides. With aliphatic alcohols in carbon disulphide solution at or below 25°C., alkyl iodides are formed.[29] With silver *iso*cyanate in nitromethane solution the reaction:

$$PI_3 + 3AgNCO \rightarrow P(NCO)_3 + 3AgI$$

commencing at room temperature and complete under reflux is reported.[30] The solubility of phosphorus(III) iodide in liquid sulphur dioxide at 25°C. is 0·3 w./w. %.[31] On heating phosphorus(III) iodide with dihydroxydifluoroboric acid, the main reaction was thought[32] to be:

$$3H_3BO_2F_2 + 2PI_3 = [B_2O_3.P_2O_3] + 6HI + BF_3 + 3HF$$

Small amounts of iodine, elementary phosphorus and an unidentified liquid product (b.p. 76°C.) were also present. With tetrasilane in a sealed tube at 100°C., a colourless spontaneously inflammable liquid of unknown composition (evolving iodine vapour on combustion) is formed.[33]

Diethyl ether on the other hand has been reported[35] to catalyze the reaction:

$$2PI_3 \rightarrow P_2I_4 + I_2$$

Phosphorus(III) iodide forms complex compounds with boron(III) bromide and iodide, but not with the less acidic fluoride and chloride.[38] The reaction with boron (III) bromide in carbon disulphide at $-40°$ yields $Br_3B,PI_3$, yellow, decomp. 50°,[49] m.p. 159–160° (decomp.).[38, 52] Similarly boron(III) iodide yields $I_3B,PI_3$, yellow or orange, decomp. below 250°,[38, 50, 52] subl. (*in vacuo*) 100°.[49] The infra-red spectrum of $I_3B,PI_3$ has been recorded,[38, 51] and is compatible with a P–B bond stretching force constant of 1·0 millidyne/A., and a P–B dissociation energy of ~16 kcal./mole.[51] Further thermodynamic data for both compounds are tabled[52] in Section XV, page 521. The compound is slightly soluble in carbon disulphide or benzene, hydrolyzed by water or atmospheric moisture with evolution of hydrogen iodide, and oxidized, slowly by dry air or rapidly by nitric acid, liberating iodine. It decomposes to cubic boron phosphide at 900°C.[50] Aluminium(III) iodide on the other hand reacts with phosphorus(III) iodide in carbon disulphide to give the dark brown solid complex $2PI_3,AlI_3$, m.p. 127–130°C., which is rapidly decomposed by polar solvents or atmospheric moisture. The complex is probably monomeric, with a trigonal bipyramidal structure (symmetry $D_{3h}$), corresponding to the unusual co-ordination number of 5 at the aluminium atom.[45] Little is known of organic co-ordination compounds of phosphorus(III) iodide except the 1:1 complex with 2-thioamidopyridine (TP) which appears to ionize in ethanolic solution[53]:

$$PI_3(TP) \rightleftharpoons [PI_2TP^+]+I^-$$

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## SECTION XVII

# THE THIOPHOSPHORYL HALIDES

BY A. F. CHILDS

## THIOPHOSPHORYL FLUORIDE AND MIXED HALIDE FLUORIDES

### Thiophosphoryl Fluoride, $PSF_3$

PREPARATION

The formation of thiophosphoryl fluoride by the action of lead(II) fluoride on tetraphosphorus decasulphide (Thorpe and Rodger, Mellor, VIII, 1071) has been confirmed, and an apparatus suitable for carrying out the reaction has been described.[1–2] A more generally applicable preparation, which can also be used to obtain mixed fluorides, is the fluorination of thiophosphoryl chloride[3] or bromide,[4–5] by antimony(III) fluoride. In the case of thiophosphoryl chloride, antimony(V) chloride is added as a catalyst, and the reaction is carried out at 75–80°C. The fluorinated products issue through a reflux head and, by controlling the temperature of reflux and the pressure within the apparatus, the proportion of the various products can be varied. The best yield of thiophosphoryl fluoride is obtained at atmospheric pressure, using solid carbon dioxide/acetone in the reflux head. The product can be purified by fractional distillation through a spiral nichrome column in a nitrogen atmosphere. The fluorination of thiophosphoryl bromide is carried out at 60–70°C.

Thiophosphoryl fluoride has also been prepared by fluorination of thiophosphoryl chloride using sodium fluoride in a polar solvent (tetramethylene sulphone, acetonitrile[6–7]) or potassium fluorosulphinate, $KSO_2F$.[8] The yield in both reactions is just over 50% of the theoretical quantity. In all cases moisture and oxygen must be strictly excluded from the apparatus in which thiophosphoryl fluoride is being prepared or handled.

PHYSICAL PROPERTIES

Thiophosphoryl fluoride is a colourless gas which can ignite spontaneously in air. It condenses to a colourless, highly refractive liquid, b.p. $-52{\cdot}3 \pm 0{\cdot}05$°C.[3] (cf. $-52{\cdot}6$°C./760 mm.[2]), and on further cooling forms a white solid, f.p. $-148{\cdot}8 \pm 0{\cdot}5$°C.[3,9] It forms a eutectic, f.p. $-152{\cdot}1 \pm 0{\cdot}5$°C., with pure boron trifluoride, but unlike phosphoryl chloride shows no evidence of compound formation.[9] The vapour pressure of the liquid is given by the relation $\log p = 7{\cdot}5882 – 1038{\cdot}8/T$ ($T$ in °K.) and the latent heat of vaporization (kcal. mole$^{-1}$) is 4·684,[3] 4·73.[2] The liquid has a normal Trouton constant (21·2,[3] 21·4[2]) and the substance is not associated in the vapour phase.[2] The critical temperature and pressure are 72·8°C. and 37·7 atm., respectively. From the measured linear Stark components in the microwave spectrum the dipole moment has been calculated to be $0{\cdot}633 \pm 3\%$ relative to carbon oxysulphide.[10]

The tetrahedral structure of symmetry $C_{3v}$ established for thiophosphoryl fluoride by electron diffraction[11] has been confirmed and refined by microwave spectroscopy.[5] The most probable values of bond lengths and angles in thiophosphoryl fluoride and other thiophosphoryl halides of which the structure is known are shown in Table I.

The P–S and P–F bond lengths observed in $PSF_3$ are significantly shorter than in other $X_3PS$ compounds, presumably due to contributions from ionic structures. Attempts have been made to relate in greater detail the variation of structure of the

Table I.—Bond Angles and Distances in Thiophosphoryl Halides

| | $PSF_3$ | $PSCl_3$ | $PSF_2Br$ | $PSFBr_2$ | $PSBr_3$ |
|---|---|---|---|---|---|
| P–S (A.) | 1·87 ± 0·03 | 1·85 ± 0·02 | 1·87 ± 0·05 | 1·87 ± 0·05 | 1·89 ± 0·06 |
| P–F (A.) | 1·53 ± 0·02 | | 1·45 ± 0·08 | 1·50 ± 0·10 | |
| P–Cl (A.) | | 2·02 ± 0·01 | | | |
| P–Br (A.) | | | 2·14 ± 0·04 | 2·18 ± 0·03 | 2·13 ± 0·03 |
| ∠F–P–F (°) | 100·3 ± 2 | | | | |
| ∠F–P–S (°) | 117·5 ± 2 | | | | |
| ∠Cl–P–Cl (°) | | 100·5 ± 1·0 | | | |
| ∠Br–P–Br (°) | | | | 100 ± 3 | 106 ± 3 |
| ∠F–P–Br (°) | | | 106 ± 3 | | |
| Method* | e, m | e, m | e | e | e, x |
| Reference | 11, 5 | 13, 5 | 12 | 12 | 12, 96 |

* e = electron diffraction, m = microwave spectroscopy, x = *X*-ray diffraction.

thiophosphoryl halides to the electronegativity of the substituent halogens,[14] but further more accurate structure determinations are required to confirm the validity of these conclusions.

The Raman spectrum of liquid thiophosphoryl fluoride shows the six lines (three polarized and three depolarized) expected for a molecule of symmetry $C_{3v}$.[15] A normal co-ordinate treatment based on the values of potential constants for similar molecules gave calculated values of the absorption frequencies agreeing to within 1% with those observed.[16] Force constants (dynes/cm. × $10^5$) $f_D = 4{\cdot}500$, $f_d$ 4·774, $f_\alpha$ 0·219, $f_\beta$ 1·425, $f_{d\alpha}$ 0·273 and $f_{\alpha\alpha}$ 0·144 have been derived similarly.[17] The infra-red spectrum of thiophosphoryl fluoride has been recorded[113] and discussed, together with the spectra of $SPF_2Cl$ and $SPF_2Br$, from the point of view of the effect of substituents on the P = S stretching frequency in the molecules.[114] The nuclear magnetic resonance data for these compounds, recorded below, can also be explained by the differing polarities of the $\sigma$ bonds and differing degrees of $\pi$ bonding.[115]

| | $SPF_3$ | $SPF_2Cl$ | $SPF_2Br$ |
|---|---|---|---|
| $^{31}P$ multiplicity | 4 | 3 | 3 |
| Coupling constant $J_{PF}$ | 1180 | 1220 | 1252 |
| $^{31}P$ chemical shift$^{(a)}$ | 32·4 | 50·0 | 28·6 |
| $^{19}F$ multiplicity | 2 | 2 | 2 |
| Coupling constant $J_{PF}$ | 1184 | 1218 | 1249 |
| $^{19}F$ chemical shift$^{(b)}$ | 51·3 | 15·9 | 2·3 |

$^{(a)}$ In p.p.m. downfield from 85% $H_3PO_4$.
$^{(b)}$ In p.p.m. upfield from $CCl_3F$.

### CHEMICAL PROPERTIES

The aqueous hydrolysis of thiophosphoryl fluoride is slow, being only 3·3% complete after 4·5 hr. at room temperature.[1] The first product of alkaline hydrolysis is a salt of phosphorodifluoridothioic acid, $HOPSF_2$, which can be precipitated as its insoluble nitron salt. Further hydrolysis gives phosphorothioic acid, $H_3PSO_3$, and finally (in acid or neutral medium) phosphoric acid. No phosphorofluoridothioic acid can be isolated.[2]

Reactions with metals, where they occur, lead to the formation of sulphides (or fluorides) and trivalent phosphorus compounds.[1] The gas has no action on mercury or nichrome in the cold, but slightly attacks copper.[3]

## Diphosphorus Tetrasulphur Tetrafluoride, $P_2S_4F_4$

This compound, b.p. 58–60°/10 mm., is prepared by bromine oxidation of the anion $S_2PF_2^-$, obtained by the action of alkali metal fluorides on tetraphosphorus decasulphide in acetonitrile (see Section XI. Its infra-red and nuclear magnetic resonance spectra are consistent with the structure $F_2(S)PSSP(S)F_2$. It reacts with *cyclo*hexene to give $C_6H_{10}[SP(S)F_2]_2$, a colourless liquid, moderately stable to hydrolysis.[116]

### Thiophosphoryl Chlorofluorides

Thiophosphoryl chlorodifluoride, $PSF_2Cl$, and thiophosphoryl dichlorofluoride, $PSFCl_2$, are obtained as intermediates in the preparation of thiophosphoryl fluoride as described above.[3, 8] They are colourless compounds, with the physical properties given in Table II. Thiophosphoryl chlorodifluoride has also been obtained in 80% yield by the action of anhydrous hydrogen chloride on *N*,*N*-diethylphosphorodifluoridothionic amide, $F_2P(S)NEt_2$.[114]

*Table II.—Physical Properties of Thiophosphoryl Chlorofluorides*

| Property | $PSFCl_2$ | $PSF_2Cl$ |
|---|---|---|
| B.p. (°C.)/760 mm. | 64·7 ± 0·05 | 6·3 ± 0·05 |
| F.p. (°C.) | −96·0 ± 0·5 | −155·2 ± 0·5 |
| Liquid density at 0°C. | 1·590 | 1·484 |
| Gas density (observed) | 169·1 | 137·3 |
| Gas density (calc.) | 153·0 | 136·6 |
| Critical temp. (°C.) | — | 166·0 |
| Critical pressure (atm.) | — | 40·9 |
| Heat of vaporization (g.-cal.) | 6863 | 5703 |
| Trouton constant | 20·3 | 20·4 |
| Vapour pressure constants *A* | 7·6596 | 7·5100 |
| (log $p=A-B/T$) *B* | 1613·9 | 1292·7 |

The observed boiling points agree closely with those calculated by the method of Maslov.[18–9] The molecular structure of the thiophosphoryl chlorofluorides has not been determined, but the Raman spectrum of liquid thiophosphoryl chlorodifluoride shows the nine frequencies expected from a molecule of symmetry $C_{1h}$.[15] The spectrum of thiophosphoryl dichlorofluoride on the other hand shows only eight absorptions, the deformation frequencies somewhat resembling those of a $C_{3v}$-type molecule, possibly because of the similarity in mass between the sulphur and chlorine atoms.[20] The infra-red spectrum of the dichlorofluoride has been determined. Absorptions at 476 and 565 cm.$^{-1}$ were assigned to P–Cl vibrations and one at 900 cm.$^{-1}$ to the P–F vibration.[21] A study of the infra-red spectra of phosphoryl and thiophosphoryl mixed halides, showed that whereas the frequency of the phosphoryl absorption depends additively on the electronegativities of the substituent halogens, simple inductive effects will not explain the behaviour of the thiophosphoryl absorption.[117]

Like thiophosphoryl fluoride, the chlorofluorides hydrolyze slowly in aqueous potassium hydroxide, or in moist air. The chlorodifluoride will also explode spontaneously in air at certain concentrations, but this behaviour has not been observed with the dichlorofluoride. The latter compound attacks mercury when hot, but neither chlorofluoride has any action on mercury or nichrome in the cold.[3] Thiophosphoryl dichlorofluoride reacts with the lower alcohols to give colourless alkyl phosphorochloridofluoridothionates, which by further treatment with sodium alkoxide yield dialkyl phosphorofluoridothionates:

$$\mathrm{PSFCl_2 + ROH \rightarrow ROPSFCl \xrightarrow{RONa} (RO)_2PSF}$$

Analogous reactions are observed in the case of primary and secondary amines, and the products are claimed to be powerful insecticides[22]:

$$\mathrm{PSFCl_2 + RR'NH \rightarrow PS(NRR')FCl \xrightarrow{R''ONa} R''OPS(NRR')F}$$

### Thiophosphoryl Bromofluorides

Thiophosphoryl bromodifluoride, $PSF_2Br$, and thiophosphoryl dibromofluoride, $PSFBr_2$, have been prepared by the fluorination of thiophosphoryl bromide by antimony(III) fluoride. Fluorination takes place smoothly and exothermically at 60–70°C., no catalyst being required. The product varies with pressure, $PSF_2Br$ being the main product at 40 mm. and $PSFBr_2$ at 15 mm.[4] In a similar way the action of antimony(III) fluoride on thiophosphoryl dibromochloride at 80–100°C. and 20–40 mm. yields a high proportion of thiophosphoryl bromochlorofluoride, PSFClBr. The same product is also obtained, in admixture with thiophosphoryl dichlorofluoride, by fluorination of thiophosphoryl bromodichloride.[20]

The three bromofluorides are colourless fuming liquids, with the physical properties given in Table III.

*Table III.—Physical Properties of Thiophosphoryl Bromofluorides*

| | $PSF_2Br$ | $PSFBr_2$ | PSFClBr |
|---|---|---|---|
| B.p. (°C.)/760 mm. | $35{\cdot}5 \pm 0{\cdot}1$ | $125{\cdot}3 \pm 0{\cdot}1$ | 97–98 |
| F.p. (°C.) | $-136{\cdot}9 \pm 0{\cdot}5$ | $-75{\cdot}2 \pm 0{\cdot}1$ | |
| Liquid density | 1·940/0°C. | 2·390/0°C. | 1·96 |
| Heat of vaporization (g.-cal.-mole$^{-1}$) | 6775 | 8351 | |
| Trouton constant | 22·0 | 21·0 | |
| Vapour pressure constants $A$ | 7·6970 | 7·4674 | |
| (log $p = A - B/T$) $B$ | 1484·8 | 1827·3 | |
| Reference | 25 | 25 | 22 |

The molecular structure which has been established by electron diffraction for thiophosphoryl dibromofluoride and bromodifluoride[12] (see Table I) conforms with the observed Raman spectra[15, 20] of these substances, which show the nine absorption frequencies expected for molecules of symmetry $C_{1h}$. The Raman spectrum of thiophosphoryl bromochlorofluoride also shows nine absorptions, but two are polarized showing that the molecule tends towards a $C_{1h}$ structure (possibly because of the similarity of Cl and S in mass) rather than the expected $C_1$ symmetry.[20]

Thiophosphoryl dibromofluoride is unaffected by standing for 24 hr. at room temperature over water or dilute potassium hydroxide solution, and reacts only slowly at the boiling point. It is miscible without reaction with acetone, carbon tetrachloride and paraffin wax. It does not react with lead, tin, zinc, nichrome or sulphur in the cold. Iron is corroded giving a white, and silver a yellow, solid respectively. Copper is severely attacked to form white, red and black solids, probably fluorides and sulphides. Mercury reacts at 70°C. to give unspecified products. Sodium iodide gives a red colour with thiophosphoryl dibromofluoride, presumably due to liberation of iodine.

Thiophosphoryl bromodifluoride is somewhat more reactive, hydrolyzing slowly in cold potassium hydroxide and vigorously in hot sodium hydroxide solution, and attacking mercury slightly at 35–40°C.[4]

## THIOPHOSPHORYL CHLORIDE AND MIXED HALIDE CHLORIDES

### Thiophosphoryl Chloride, $PSCl_3$

PREPARATION

Many of the methods described in the earlier literature (Mellor, VIII, 1074) have been developed further for the laboratory or commercial preparation of thiophosphoryl chloride. The most generally applicable of these is the addition of sulphur to phosphorus trichloride. The second order reaction between the pure materials is slow at 100°C., and even under increased pressure at 200°C. requires 7–8 hr. for its completion.[24–5] To avoid the use of increased pressure it has been proposed to bubble phosphorus trichloride vapour through a heated solution of sulphur in an inert solvent of high boiling point.[26] However, the reaction is better carried out at lower temperatures using a catalyst, of which the best is probably aluminium chloride.[27] The presence of only 1–2 moles % of this substance leads to complete reaction of sulphur with phosphorus trichloride in 10 min. at 100°C. and atmospheric pressure. A useful laboratory preparation of thiophosphoryl chloride, based on this procedure, has been reported[28] and variants of it have been patented[29–30] including the use of ferric chloride or aluminium bromide as catalysts.[31–2] Other catalysts which have been suggested include metals,[33] activated carbon,[34–5] sodium sulphide[24] and sulphur monochloride.[36]

The thiohydrolysis of phosphorus pentachloride first described by Sérullas (Mellor, VIII, 1074) has been studied both in liquid hydrogen sulphide[37] and in carbon disulphide solution,[38] the yield of thiophosphoryl chloride in the latter case being only 70%:

$$PCl_5 + H_2S \rightarrow PSCl_3 + 2HCl$$

The interaction of carbon tetrachloride and tetraphosphorus decasulphide is also claimed to give thiophosphoryl chloride in 60% yield[39]:

$$3CCl_4 + P_4S_{10} \rightarrow 4PSCl_3 + 3CS_2$$

This reaction is interesting in being the complement of that described by Carius (Mellor, VIII, 1074):

$$2PCl_5 + CS_2 \rightarrow CCl_4 + 2PSCl_3$$

The two together lead to the overall reaction:

$$6PCl_5 + P_4S_{10} \rightarrow 10PSCl_3$$

which has received little attention since its discovery by Weber (Mellor, *loc. cit.*), although it has been suggested as a laboratory preparation.[40] (The reaction will also yield condensed thiophosphoryl halides under suitable conditions.[109]) Thiophosphoryl chloride, amongst other products, has also been claimed to result from the reaction of sulphur monochloride, either with ferrophosphorus[41]:

$$Fe_2P + 3\tfrac{1}{2}S_2Cl_2 \rightarrow 2FeCl_2 + PSCl_3 + 6S$$

with phosphorus trichloride and tetraphosphorus decasulphide[42]:

$$18PCl_3 + P_4S_{10} + 6S_2Cl_2 \rightarrow 22PSCl_3$$

or with calcium phosphate, silica and carbon at 1000°C.[43] A procedure which involves elements of several of the above consists in causing sulphur, phosphorus and chlorine to react directly in a heel of thiophosphoryl chloride, using wood charcoal as catalyst.[44] Thiophosphoryl chloride is also obtained by the interaction of thiophosphoryl nitride with hydrogen chloride[118]:

$$PNS + 4HCl \rightarrow PSCl_3 + NH_4Cl$$

Several preparations of radioactive thiophosphoryl chloride have been described. Thus $^{31}P^{35}SCl_3$,[45–6] $^{32}P^{32}SCl_3$[47–8] and $^{32}P^{35}SCl_3$,[49] have all been prepared by interaction of appropriately labelled sulphur and phosphorus trichloride. Neutron irradiated phosphorus trichloride contains $^{31}P^{35}SCl_3$ and $^{32}P^{35}SCl_3$, the radioisotopes being formed by the $^{31}P(n,\gamma)^{32}P$ and $^{35}Cl(n,p)^{35}S$ reactions.[50–1] Less than 2% exchange takes place in $S/P^{35}SCl_3$ and $S_2Cl_2/P^{35}SCl_3$ mixtures,[51] but 60% exchange of $^{32}P$ takes place between $H^{32}PO_4$ and $PSCl_3$ in 60 hr. at 150°C.[52]

## PHYSICAL PROPERTIES

Thiophosphoryl chloride exists in two solid forms. When warmed the $\alpha$-form, f.p. $-40{\cdot}8 \pm 0{\cdot}2$°C., is transformed with evolution of heat to the $\beta$-form, f.p.

$-36{\cdot}2 \pm 0{\cdot}2$°C.[3] A redistilled specimen of the liquid had b.p. 125·0°C., $n_D^{25}$ 1·5432, $d_4^{25}$ 1·6271.[53] Other values ($n_D^{20}$ 1·5554, $d_4^{20}$ 1·6369[54]) seem in better accord with previous determinations (Mellor, VIII, 1074, 1075) and lead to a value of $MR_L$ 33·25 close to that obtained by summing the bond refractivities P–Cl = 8·856, P=S = 6·866.[55] The observed (263·63) and calculated (259·97) bond refraction constants, $MR_E$,[55–6] are also in good agreement.

Values of the density and viscosity of thiophosphoryl chloride at various temperatures are tabulated below:

| $d_4^t$ (g./c.c.) | $t$ (°C.) | $\eta$ (centipoise) |
|---|---|---|
| 1·734 | −30·4 | 2·627 |
| 1·703 | −20·4 | 2·102 |
| 1·687 | −10·0 | 1·741 |
| 1·679 | −5·4 | 1·605 |
| 1·673 | 0·0 | 1·496 |
| 1·621 | +25·0 | 1·017 |
| 1·590 | +45·0 | 0·806 |
| 1·559 | +65·0 | 0·665 |
| 1·542 | +75·0 | 0·611 |
| 1·531 | +85·0 | 0·569 |
| 1·513 | +98·5 | 0·519 |

The complex viscosity behaviour of the chloride near its melting point is surprising, in view of the simple behaviour of $PCl_3$ and $POCl_3$ under similar conditions. The ratio of the energy of vaporization to the activation energy for viscous flow is anomalously high at higher temperatures, and it has been suggested that both these phenomena can be explained by evoking an easy flow process for the approximately spherical $PSCl_3$ molecule in the "normal" region.[119]

The relative molar magnetic rotivity[57] of thiophosphoryl chloride $[\Omega]_M$ for light of wave-length 5460 A. at 20°C. is $676 \times 10^{-2}$ min. and the corresponding molar magnetic rotation ($[\rho]_M$) is $944 \times 10^{-2}$ min. The contribution of the sulphur atom to magnetic rotation, $\Delta[\rho]_M = \rho PSCl_3 - \rho PCl_3$ is positive ($157 \times 10^{-2}$ min.).[54]

Liquid thiophosphoryl chloride is miscible with benzene, carbon tetrachloride, carbon disulphide and chloroform.[40] Although its donor properties towards antimony(V) chloride and tin(IV) chloride are inferior to those of phosphoryl chloride,[58] it is nevertheless a powerful solvent for Lewis acids as can be seen from Table IV.

*Table IV.—Solubility of Inorganic Halides in Thiophosphoryl Chloride*

| Halide | Solubility* | Colour of solution |
|---|---|---|
| $AlCl_3$ | 30·65 | light yellow |
| $SnCl_4$ | miscible | colourless |
| $SbCl_3$ | 125·3 | colourless |
| $TiCl_4$ | miscible | yellow |
| $FeCl_3$ | 7·26 | greenish-red |
| $AsCl_3$ | miscible | colourless |
| $BiCl_3$ | 0·52 | colourless |
| $BCl_3$ | miscible | colourless |
| $SbCl_5$ | moderate | — |
| $ZrCl_4$ | slight | — |
| $TeCl_4$ | slight | — |

* g./100 g. $PSCl_3$ at 35°C. where known.

The compounds $AlCl_3$,$PSCl_3$ (yellowish, m.p. 115°C. (decomp.)) and $SbCl_3$,$PSCl_3$ (red-brown, m.p. 101°C. (decomp.)) separate from saturated solution. Lithium, sodium, potassium, ammonium and barium chlorides are all soluble to less than 0·1%.

Dimethylaniline and γ-picoline are very soluble in the solvent, quinoline, pyridine and α- and β-picoline moderately soluble. By neutralization of the appropriate solvo-acids and bases the complexes shown in Table V were obtained.[59] The authors assume from this that thiophosphoryl chloride ionizes in the sense:

$$PSCl_3 \rightleftharpoons PSCl_2^+ + Cl^-$$

This is supported by a study of the electrolysis of solutions of radioactive iron(III) chloride in thiophosphoryl chloride. Unlike phosphoryl chloride where a complex iron-containing cation was observed, thiophosphoryl chloride ionized ferric chloride in the sense[120]:

$$PSCl_3 + FeCl_3 \rightarrow [PSCl_2^+][FeCl_4^-]$$

*Table V.—Complexes Resulting from Reactions in Thiophosphoryl Chloride*

| Complex | Colour | m.p. °C. (uncorr.) |
|---|---|---|
| $(C_9H_7NPSCl_2)(SbCl_6)$ | brown | 150–3 |
| $(C_5H_5NPSCl_2)(SbCl_6)$ | brown | 120–2 (decomp.) |
| $(\beta\text{-}C_6H_7NPSCl_2)(SbCl_6)$ | red brown | 142–3 (decomp.) |
| $(C_9H_7NPSCl_2)(AlCl_4)$ | white | 100–2 |
| $(C_5H_5NPSCl_2)(AlCl_4)$ | white | 133–5 |
| $(C_9H_7NPSCl_2)_2(SnCl_6)$ | white | 200 (decomp.) |
| $(C_5H_5N)_2PSCl_3SnCl_4$ | white | — |
| $(\alpha\text{-}C_6H_7N)_2PSCl_3SnCl_4$ | pale yellow | 160–2 |
| $(\gamma\text{-}C_6H_7N)_2PSCl_3SnCl_4$ | white | 180 |
| $C_9H_7NPSCl_3TiCl_4$ | orange red | 210–5 |
| $(C_5H_5N)_2PSCl_3TiCl_4$ | yellow | 175–9 (decomp.) |

The structure of the thiophosphoryl chloride molecule has been determined by electron diffraction[13] and microwave spectroscopy,[5] the results being given in Table I. The $C_{3v}$ symmetry exhibited by the molecule is in accord with the Raman spectrum which has been observed by several authors. These observations have been collated and used to calculate values of the heat content, entropy, free energy and heat capacity for the ideal gaseous state at 1 atm. pressure[16] (see Table VI). These are in broad agreement with previous data,[60–1] based on an earlier structure determination.[13]

*Table VI.—Thermodynamic Data for Thiophosphoryl Chloride*

| $T$°K. | $\dfrac{H^\circ - E^\circ}{T}$ | $-\dfrac{G^\circ - E^\circ_0}{T}$ | $S^\circ$ | $C^\circ_p$ |
|---|---|---|---|---|
| 200 | 12·78 | 59·48 | 72·53 | 18·57 |
| 250 | 14·12 | 62·75 | 76·87 | 20·28 |
| 273·16 | 14·67 | 64·02 | 78·69 | 20·90 |
| 298·16 | 15·22 | 65·33 | 80·55 | 21·47 |
| 300 | 15·26 | 65·43 | 80·68 | 21·51 |
| 400 | 17·03 | 70·07 | 87·11 | 23·07 |
| 500 | 18·34 | 74·02 | 92·36 | 23·94 |
| 600 | 19·32 | 77·45 | 96·77 | 24·47 |
| 700 | 20·08 | 80·50 | 100·59 | 24·80 |
| 800 | 20·68 | 83·21 | 103·90 | 25·03 |
| 900 | 21·18 | 85·68 | 106·86 | 25·19 |
| 1000 | 21·58 | 87·95 | 109·54 | 25·31 |

A thermochemical study of the aluminium chloride catalyzed addition of sulphur to phosphorus(III) chloride led to a value of −79·2 kcal./mole for the heat of formation of liquid thiophosphoryl chloride at 25°C. From this a value of 61–70 kcal./mole was deduced for the heat of dissociation of the P═S bond, a value significantly lower than those suggested by earlier workers.[121]

The infra-red spectrum of thiophosphoryl chloride has also been reported by several authors.[24, 62–3] The three fundamental frequencies, 430, 540 and 753 cm.$^{-1}$, are in good agreement with the corresponding Raman values[16] and in the vapour spectrum two of the fundamentals show contours characteristic of the 'parallel' bands of a 'symmetrical-top' molecule.[62]

The infra-red absorption spectrum of a mixture of thiophosphoryl chloride and carbon disulphide exhibits a system of bands due to simultaneous transitions with some frequencies of both molecules. This molecular 'simultaneous transition spectrum' is analogous to the Raman spectrum but shifted to higher frequencies by the 1515 cm.$^{-1}$ of the $\nu_3$ carbon disulphide band. It is limited by the transparency region of carbon disulphide (1500–2100 cm.$^{-1}$) to molecular frequencies between *ca.* 160 and 500 cm.$^{-1}$ The three simultaneous transition frequencies observed for thiophosphoryl chloride[64] (168, 249, 430 cm.$^{-1}$) agree well with Raman data[16] (169, 247, 431 cm.$^{-1}$).

The polarization of thiophosphoryl chloride in benzene or heptane solutions at infinite dilution is 74·3 and the dipole moment of the molecule 1·41 D., whence the P–S bond moment is calculated as 2·5 D.[53] (2·23 D.[65]). The force constant of the P–S bond has been calculated as $5{\cdot}36 \times 10^5$ dynes/cm.[66–7] (see also reference 68). On the basis of Raman data the P–S bond order is calculated as 1·57[69] from the equation: Bond order $(N) = 0{\cdot}61(f_N/f_1) + 0{\cdot}37$, where $f_1$ is given by the 'Product rule'.[70]

The $^{31}$P nuclear magnetic resonance spectrum of thiophosphoryl chloride shows a chemical shift of −28·8 p.p.m. referred to 85% phosphoric acid[71–2]; earlier workers[73–4] reported slightly higher values.

### CHEMICAL PROPERTIES

Thiophosphoryl chloride does not attack nichrome or mercury at room temperature, but reacts with mercury when heated. It is stable in moist air, but hydrolyzes slowly in potassium hydroxide solution. Antimony(III) fluoride causes successive replacement of the chlorine atoms by fluorine.[3] Other inorganic fluorides (sodium fluoride, potassium fluorosulphinate) have also been used[6–8] (see page 534), although nitrosyl fluorosulphinate does not react.[75] The action of dry oxygen on thiophosphoryl chloride was negligible over 26 years, as measured by pressure decrease or sulphur deposition.[76] Sulphur trioxide oxidizes the chloride with liberation of sulphur.[59]

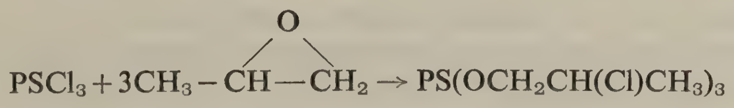
Thiophosphoryl chloride reacts with most aliphatic alcohols giving alkyl phosphorodichloridothionates[77]:

$$PSCl_3 + ROH \rightarrow ROPSCl_2 + HCl$$

The reaction can also be applied to unsaturated alcohols (allyl alcohol[38]), but the interaction of 1,3-dichloropropan-2-ol and thiophosphoryl chloride at 150°C. gives no recognizable products.[78] In the presence of sodium hydroxide,[79] or by the use of aluminium alkoxides,[80] dialkyl phosphorochloridothionates are obtained:

$$2ROH + PSCl_3 + 2NaOH \rightarrow (RO)_2PSCl + 2NaCl + 2H_2O$$
$$3PSCl_3 + 2Al(OR)_3 \rightarrow 3(RO)_2PSCl + 2AlCl_3$$

Olefin oxides react with thiophosphoryl chloride to give tris-2-chloroalkyl phosphorothionates,[81] e.g.



$$PSCl_3 + 3CH_3-\overset{O}{CH-CH_2} \rightarrow PS(OCH_2CH(Cl)CH_3)_3$$

Certain tervalent phosphorus compounds, such as phenyldichlorophosphine, triaryl phosphites, diaryl phosphorochloridites[82] or aryl phosphorodichloridites,[83] will abstract the sulphur from thiophosphoryl chloride yielding the corresponding thionate esters and phosphorus trichloride, e.g.:

$$(PhO)_3P + PSCl_3 \rightarrow (PhO)_3PS + PCl_3$$

Certain alkyl esters of pentavalent phosphorus, on the other hand, undergo dealkylation[84]:

$$(R_2N)_2POOR' + PSCl_3 \rightarrow (R_2N)_2POOPSCl_2 + R'Cl$$

The reaction of Grignard reagents with thiophosphoryl chloride unexpectedly gives tetra-alkyldiphosphine disulphide[85] together with traces of trialkylphosphine sulphide and other materials.[86]

### USES OF THIOPHOSPHORYL CHLORIDE

The uses of thiophosphoryl chloride have been reviewed.[87] It is an intermediate in the manufacture of organophosphorus insecticides, especially parathion (diethyl *p*-nitrophenyl phosphorothionate). Lubricant[88–9] and fuel additives[90] based on thiophosphoryl chloride have also been proposed, and its reaction products with polystyrene are claimed as ion exchange resins.[91] The vapour of thiophosphoryl chloride is very effective in reducing the velocity of propagation of laminar flames of hydrogen or hydrocarbon–air mixtures.[92]

## Thiophosphoryl Bromochlorides

Thiophosphoryl bromodichloride, $PSCl_2Br$, and thiophosphoryl dibromochloride, $PSClBr_2$, are formed by the equilibration of mixtures of thiophosphoryl bromide and chloride at temperatures around 200°C. for several hours.[25, 63, 72] A quantitative study of the system by nuclear magnetic resonance spectroscopy shows that its behaviour approaches that calculated for completely random reorganization. The system can be defined by two equations:

$$2PSCl_2Br \rightleftharpoons PSCl_3 + PSClBr_2 \qquad (1)$$

$$2PSClBr_2 \rightleftharpoons PSBr_3 + PSCl_2Br \qquad (2)$$

for which equilibrium constants $K_1$ and $K_2$ can be written:

$$K_1 = \frac{[PSCl_3][PSClBr_2]}{[PSCl_2Br]^2}$$

$$K_2 = \frac{[PSBr_3][PSCl_2Br]}{[PSClBr_2]^2}$$

For the completely random reorganization of a mixture of bromide and chloride in which the Cl/Br atomic ratio is $p/q$ (where $p+q=1$) the probability of a phosphorus atom being attached to $n$ chlorine and $3-n$ bromine atoms is

$$P_{3(n)} = \frac{3!}{n!(3-n)!}\, p^n q^{3-n}$$

By substitution in the equation for $K_1$ and $K_2$ above, $p$ and $q$ are eliminated, giving

$$K_1 = K_2 = \tfrac{1}{3}$$

The experimentally observed values were $K_1 = 0{\cdot}297$, $K_2 = 0{\cdot}419$.

The optimum yields of bromodichloride or dibromochloride are obtained by heating thiophosphoryl chloride and thiophosphoryl bromide in a 2:1 or 1:2 mole ratio, respectively, according to the equations:

$$2PSCl_3 + PSBr_3 \rightleftharpoons 3PSCl_2Br \qquad (3)$$

$$PSCl_3 + 2PSBr_3 \rightleftharpoons 3PSClBr_2 \qquad (4)$$

The corresponding equilibrium constants of formation, $K_{PSCl_2Br}$ and $K_{PSClBr_2}$ are related to $K_1$ and $K_2$:

$$K_{PSCl_2Br} = \frac{1}{K_1{}^2K_2}$$

$$K_{PSClBr_2} = \frac{1}{K_2{}^2K_1}$$

i.e. in the ideal case the formation constant should have the value 27. From the experimental values for $K_1$ and $K_2$, $K_{PSCl_2Br} = 27{\cdot}5$ and $K_{PSClBr_2} = 20{\cdot}8$, i.e. relatively the bromodichloride is stable and the dibromochloride unstable with respect to trichloride and tribromide. Equilibrated mixtures corresponding to equations (3) and (4) above contain 46% of thiophosphoryl bromodichloride and 42% of thiophosphoryl dibromochloride respectively.[72] Later work by the same authors[93] has shown that similar reorganization occurs in heated mixtures of phosphoryl bromide and thiophosphoryl chloride to give all the eight possible phosphoryl/thiophosphoryl bromide/chlorides. The equilibrium constants derived are in satisfactory agreement with the earlier values. Similar results are obtained by the addition of sulphur to a mixture containing phosphorus dibromochloride and bromodichloride,[63] or by heating phosphorus trichloride and tribromide with sulphur at 190°C. for 5 hr.[25] An alternative, less attractive, method of preparation is the action of hydrogen sulphide on a heated mixture of phosphorus pentachloride and pentabromide.[25]

Thiophosphoryl bromodichloride and dibromochloride are isolated from such mixtures by fractional distillation (under reduced pressure to avoid decomposition). They are oily fuming liquids, with the properties given in Table VII.

*Table VII.—Physical Properties of Thiophosphoryl Bromochlorides*[63]

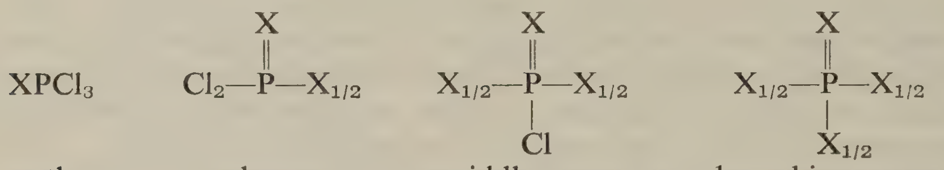
| | $PSCl_2Br$ | $PSClBr_2$ |
|---|---|---|
| Colour | colourless | pale yellow |
| B.p. (°C.) | 154–6°/731 mm.<br>45°/13 mm. | 170–175°/755 mm. (decomp.)<br>67°/13–14 mm.<br>61°/11–12 mm. |
| $d_4^{20}$ | 2·037 | 2·407 |
| $n_D^{20}$ | 1·6107 | 1·6660 |
| $^{31}P$ NMR chemical shifts* | +14·5 | +61·4 |

* p.p.m. referred to 85% $H_3PO_4$.[72]

The structure of the thiophosphoryl bromochlorides has not been determined. The Raman spectrum of thiophosphoryl bromodichloride shows only seven absorptions: as in the case of thiophosphoryl dichlorofluoride the similarity in mass of chlorine and sulphur leads to a pseudo-$C_{3v}$ symmetry where the deformation vibrations are concerned. For similar reasons the nine absorption frequencies exhibited by thiophosphoryl dibromochloride have an arrangement suggesting $C_{2v}$ rather than $C_{1h}$ symmetry.[25] The infra-red spectra,[63] with their three fundamental frequencies respectively at 740, 531 and 490 cm.$^{-1}$ ($PSCl_2Br$) and 730, 506 and 436 cm.$^{-1}$ ($PSClBr_2$), are in good agreement with the Raman data. The $^{31}P$ nuclear magnetic resonance chemical shifts are given in Table VII.[72]

## Polythiophosphoryl Chlorides

Apart from the thiopyrophosphoryl chloride, $P_2O_2SCl_4$, described by Besson (Mellor, VIII, 1023), there has been little study of compounds in which one or more of the oxygen atoms of pyrophosphoryl chloride are replaced by sulphur. A considerable advance was made by the demonstration of dithionopyrophosphoryl chloride, $Cl_2P(S)OP(S)Cl_2$, amongst the products obtained by heating together phosphoryl and thiophosphoryl chlorides, phosphorus pentoxide and tetraphosphorus decasulphide in various proportions.[100] The theory of 'random reorganization', first developed to explain the behaviour of phosphate melts,[108] can be applied to the halide system.[100] It states that, at a sufficiently high temperature, the groups attached to a given phosphorus atom exchange with those attached to other phosphorus atoms, each phosphorus retaining its co-ordination number of 4. The system can be described in terms of four elementary structures:

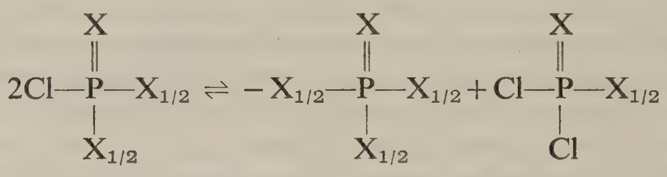


$$\mathrm{XPCl_3} \qquad \mathrm{Cl_2{-}\overset{\overset{X}{\|}}{P}{-}X_{1/2}} \qquad \mathrm{X_{1/2}{-}\underset{\underset{Cl}{|}}{\overset{\overset{X}{\|}}{P}}{-}X_{1/2}} \qquad \mathrm{X_{1/2}{-}\underset{\underset{X_{1/2}}{|}}{\overset{\overset{X}{\|}}{P}}{-}X_{1/2}}$$

ortho | end group | middle group | branching group

*o* | *e* | *m* | *b*

(where X in this case represents either oxygen or sulphur) and be completely defined by the two equilibria:

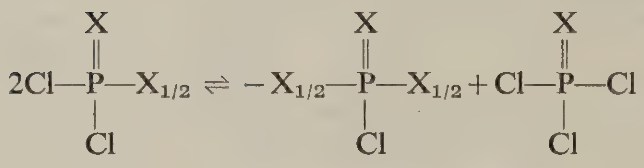


$$\mathrm{2Cl{-}\underset{\underset{X_{1/2}}{|}}{\overset{\overset{X}{\|}}{P}}{-}X_{1/2}} \rightleftharpoons \mathrm{-X_{1/2}{-}\underset{\underset{X_{1/2}}{|}}{\overset{\overset{X}{\|}}{P}}{-}X_{1/2} + Cl{-}\underset{\underset{Cl}{|}}{\overset{\overset{X}{\|}}{P}}{-}X_{1/2}}$$

$$2m = b + e$$

$$\left(K_1 = \frac{[b][e]}{[m]^2}\right)$$

and



$$\mathrm{2Cl{-}\underset{\underset{Cl}{|}}{\overset{\overset{X}{\|}}{P}}{-}X_{1/2}} \rightleftharpoons \mathrm{-X_{1/2}{-}\underset{\underset{Cl}{|}}{\overset{\overset{X}{\|}}{P}}{-}X_{1/2} + Cl{-}\underset{\underset{Cl}{|}}{\overset{\overset{X}{\|}}{P}}{-}Cl}$$

$$2e = m + o$$

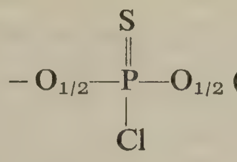
$$K_2 = \frac{[m][o]}{[e]^2}$$

Obviously the molecular complexity of the system depends on the ratio of chlorine to phosphorus atoms, $[Cl]/[P] = R$. Thus in the simple oxygen system (viz., $P_4O_{10}/POCl_3$), when $R = 3$, only orthophosphoryl chloride molecules, $POCl_3$, are present. By reorganization of mixtures having progressively decreasing values of $R$ some pyrophosphoryl chloride is first formed, followed by straight chain, branched chain and cyclic polymers of increasing molecular weight, until at $R = 1{\cdot}20$ a rubbery high polymer finally results.

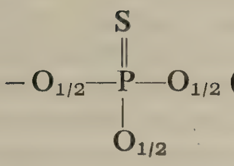
As might be expected, the behaviour of the mixed sulphur/oxygen system is more complex. Equilibration of mixtures of $POCl_3$, $PSCl_3$, $P_4O_{10}$ and $P_4S_{10}$ ($R = 1{\cdot}50$ to $2{\cdot}00$) in sealed tubes at 230°C. for ca. 65 hr. gave homogeneous liquid products only when the molar ratio of sulphur to phosphorus was 1. Compositions containing higher or lower proportions of sulphur were solid–liquid mixtures. The liquid portions of such mixtures were examined by nuclear magnetic resonance spectroscopy. When only oxygen was present ($[S]/[P] = 0$) four main $^{31}P$ NMR absorptions were observed, having chemical shifts in the range $-2$ to $+56$ p.p.m. relative to 85% $H_3PO_4$. As oxygen was progressively replaced by sulphur this group of absorptions diminished in intensity and was supplanted by a group in the range $-30$ to $+2$ p.p.m., the change being complete at $[S]/[P] = 1$. At still higher sulphur contents, the second group of absorptions was in its turn supplanted by a third group in the range $-30$ to $-65$ p.p.m. Some of these absorptions were assigned to individual structural units.

Thus a resonance at ca. −29 p.p.m. due to $PSCl_3$[71] was overlain by one at ca. −28 p.p.m., thought to be due to the end group $Cl_2P(S)-O_{1/2}$. Other tentative assignments included:

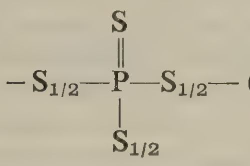
$Cl_2P(O)-S_{1/2}$ (−10 p.p.m.),



$-O_{1/2}-\underset{\underset{Cl}{|}}{\overset{\overset{S}{\|}}{P}}-O_{1/2}$ (−20 p.p.m.),



$-O_{1/2}-\underset{\underset{O_{1/2}}{|}}{\overset{\overset{S}{\|}}{P}}-O_{1/2}$ (−2 p.p.m.), and



$-S_{1/2}-\underset{\underset{S_{1/2}}{|}}{\overset{\overset{S}{\|}}{P}}-S_{1/2}-$ (−60 p.p.m.)[100],

By high vacuum distillation of a mixture having S/P mole ratio = 1 and Cl/P mole ratio 1·8, dithionopyrophosphoryl chloride, $Cl_2P(S)OP(S)Cl_2$, was isolated. The NMR spectrum of the distillate showed that 99% of the total phosphorus was present in a structure resonating at ca. −28 p.p.m. and the analysis and molecular weight determinations were in reasonable agreement with the structure postulated.[100] A subsequent attempt to make dithionopyrophosphoryl chloride by the interaction of tetraphosphorus hexaoxytetrasulphide with phosphorus pentachloride or with phosphorus trichloride and chlorine gave only the monothiono compound (see later), but dithionopyrophosphoryl chloride resulted in 5–10% yield from the interaction of commercial phosphorus pentasulphide (which contains some oxygen) with 10 molar proportions of thiophosphoryl chloride or 1 molar proportion of phosphoryl chloride at 200–240°C. for 2–3 days.[109]

The redistilled chloride had b.p. 35–38°C./0·2 mm., $n_D^{25}$ 1·5810, $d_4^{25}$ 1·731, $MR_L$ 54·3 (cf. dithionopyrophosphoryl chloride 55·4, thiolothionopyrophosphoryl chloride ($Cl_2P(O)SP(S)Cl_2$) 56·4. The infra-red absorption spectrum was assigned as follows: 935, 908 cm.$^{-1}$ (P–O–P), 764, 758 cm.$^{-1}$ (P=S), 567, 472 cm.$^{-1}$ (Cl in $-PSCl_2$). Weak absorptions at 1320 and 610 cm.$^{-1}$ were possibly due to the presence of some thionopyrophosphoryl chloride. A strong absorption at 805 cm.$^{-1}$ was unexplained. The NMR spectrum showed a single resonance at −28·4 p.p.m.[109] Thionopyrophosphoryl chloride, $Cl_2P(O)OP(S)Cl_2$, has been prepared in a similar manner, by the reorganization of mixtures of phosphorus pentoxide and thiophosphoryl chloride[109–10], of tetraphosphorus decasulphide and phosphoryl chloride[109] or of tetraphosphorus hexaoxytetrasulphide and phosphorus pentachloride.[109] The compound is distilled off under high vacuum ($10^{-3}$ mm.), and can then be redistilled with little or no decomposition at somewhat higher pressure (b.p. 34–37°C./0·2 mm., 93°C./11 mm., 99–100°C./15 mm.). It is a colourless oily liquid $n_D^{20}$ 1·5369,[110] $n_D^{25}$ 1·5340, $d_4^{25}$ 1·742.[109] A molecular weight determination shows it to be non-associated in benzene solution. The infra-red spectrum shows absorptions at 1315 cm.$^{-1}$ (P=O), 751 cm.$^{-1}$ (P=S), 934, 912 cm.$^{-1}$ (P–O–P), 652 cm.$^{-1}$ ((S)P–Cl) and 608 cm.$^{-1}$ ((O)P–Cl).[110] In another preparation the spectrum was similar except that a doublet was observed at 764 and 758 cm.$^{-1}$ and a strong unexplained absorption at 805 cm.$^{-1}$ [109] The NMR spectrum of a substantially pure specimen of thionopyrophosphoryl chloride showed two strong resonances at +10·8 p.p.m. and −30·3 p.p.m.[109] approximating to values previously assigned[100] to the $Cl_2P(O)O$ and $Cl_2P(S)O$ groups, respectively. Thionopyrophosphoryl chloride is soluble in benzene, *cyclo*hexane, carbon tetrachloride, chloroform, carbon disulphide, ether, and in other phosphorus halides. It is converted by ethanol and pyridine to the known tetraethyl thionopyrophosphate,

$$(C_2H_5O)_2P(S)OP(O)(OC_2H_5)_2$$ [110]

A compound analyzing approximately for dithiotetraphosphoryl hexachloride ($P_4O_5S_2Cl_6$) has been claimed as a by-product in the preparation of thionopyrophosphoryl chloride. A value of 477 (calc. 481) was given for the molecular weight.

The colourless viscous liquid had b.p. 82°C./$10^{-3}$ mm. (decomp.), $n_D^{20}$ 1·5533, and the infra-red spectrum gave evidence for the presence of P=O, P=S, P–Cl and P–O–P groups. However, no clearly defined organic derivatives could be isolated[110] and since a repetition of the work gave a mixture with a varying refractive index,[109] further study is required before the existence of dithiotetraphosphoryl hexachloride can be regarded as definitely established.

The thiolopyrophosphoryl chloride, $Cl_2P(O)SP(O)Cl_2$, described by Besson (*loc. cit.*) also needs further investigation. The reaction of phosphoryl chloride under reflux with hydrogen sulphide or zinc sulphide, or in a sealed tube at 150–200°C. with zinc or barium sulphide, gave none of the required product. Phosphoryl chloride reacted with hydrogen sulphide in an autoclave (100°C. for 8 days) to give mixtures of varying proportions of thionopyrophosphoryl chloride, pyrophosphoryl chloride and higher condensed chlorides.[109] The preparation of thiolopyrophosphoryl chloride has been claimed by other authors[100] but no details were given, and in view of the statement in the same paper that 'sulphur preferentially locates in the non-bridging position in poly(phosphoryl–thiophosphoryl) chloride equilibrium mixtures' it seems likely that thiolopyrophosphoryl chloride, even if it exists, will readily decompose on distillation. This is in accord with the observation that tetra-alkyl thiopyrophosphates exist in the thiono- and not in the thiolo- form.[111] Attempts to isolate trithiopyrophosphoryl chloride by the reaction of tetraphosphorus decasulphide with thiophosphoryl chloride have been similarly unsuccessful.[109] To summarize, therefore, it seems that all condensed thiopyrophosphoryl chlorides, even the mono- and dithiono- compounds which are the best established, readily decompose or rearrange on heating, yielding a wide range of products in mobile equilibrium with one another.

## THIOPHOSPHORYL BROMIDES

### Thiophosphoryl Bromide, $PSBr_3$

PREPARATION

The interaction of phosphorus pentabromide and tetraphosphorus decasulphide (Mellor, VIII, 1076) has been recommended for the laboratory preparation of thiophosphoryl bromide.[23] The product is purified by distillation under reduced pressure and washing with very dilute aqueous potassium bromide. The bromination of tetraphosphorus trisulphide or heptasulphide, however, yields a mixture of thiophosphoryl bromide, diphosphorus hexathiodibromide and diphosphorus pentathiotetrabromide[99, 107] (see pages 547–8). Later workers claim that the addition of excess sulphur to phosphorus tribromide is a superior procedure. The reaction is carried out under nitrogen at 130°C. and the distilled product recrystallized from dry ligroin at −30°C.[63] Aluminium bromide has been claimed to catalyze the addition.[94] Thiophosphoryl bromide also results from the thiohydrolysis of phosphorus pentabromide[12]:

$$PBr_5 + H_2S \rightarrow PSBr_3 + 2HBr$$

and, in small quantities, from the reorganization of mixtures of phosphoryl bromide and thiophosphoryl chloride.[93] $^{32}P^{32}SBr_3$ has been prepared by the addition of bromine to a suspension of red phosphorus ($^{32}P$), sulphur and aluminium chloride, in carbon disulphide.[95]

PHYSICAL PROPERTIES

Thiophosphoryl bromide is a pale yellow crystalline solid with a pungent odour, m.p. 38·2°C., b.p. 212°C. (decomp.), 125–130°C./25 mm., 95–96°C./18 mm.[23, 63] The crystals are cubic with $a = 11{\cdot}03$ A. and there are 8 molecules in the unit cell. The space group is $T_h^6$-*Pa*3 and the general structure is similar to that of tin(IV) iodide, with P and S lying on 3-fold axes. The measured density is 2·97 (calc. 2·99) g./c.c.[96] The vapour pressure of the solid between 0 and 36·2°C. is given by the relation $\log p = -(3196{\cdot}2/T) + 10{\cdot}105$ mm. and that of the liquid between 40·4 and 80·6°C.

by $\log p = -(2614{\cdot}9/T) + 8{\cdot}3383$ mm.[97] Values for the heat content, standard free energy and standard entropy changes involved in various phase transitions, and quoted by the same authors, are given in Table VIII.

*Table VIII.—Thermodynamic Data for Phase Changes in Thiophosphoryl Bromide*

| Phase change | $\Delta H$ kcal./mole | $\Delta G$ g.-cal./mole | $\Delta G_{298{\cdot}1}$ kcal./mole | $\Delta S_{298{\cdot}1}$ kcal./mole |
|---|---|---|---|---|
| $[PSBr_3]_s \rightarrow PSBr_3$ | 14·62 | 14621–46·208 $T$ | 0·850 | 46·20 |
| $[PSBr_3]_l \rightarrow PSBr_3$ | 12·09 | 12089–38·155 $T$ | 0·715 | 38·15 |
| $[PSBr_3]_s \rightarrow [PSBr_3]_l$ | 2·53 | 2532–8·053 $T$ | 0·135 | 8·05 |

The liquid dissolves sulphur and is itself soluble in phosphorus trichloride, chloroform, ether, carbon disulphide or ligroin. The solid may be recrystallized from the last two solvents.

The molecular arrangement in crystalline thiophosphoryl bromide is described above, and the structure of the molecule itself, as deduced from *X*-ray and electron diffraction measurements, is given in Table I.[12, 96] The Raman spectrum[25] shows the six frequencies corresponding to the expected $C_{3v}$ symmetry. The three fundamental infra-red absorptions,[63] 723, 472 and 321 cm.$^{-1}$, occur at a higher frequency than the respective Raman absorptions (718, 438 and 299 cm.$^{-1}$). Later authors place the six fundamental absorptions at 726, 431, 299, 175, 165 and 133 cm.$^{-1}$, and hence deduce values for reduced enthalpy, reduced free enthalpy, entropy and molar heat capacity at 100° intervals from 200–2000°K.[122] The $^{31}$P chemical shift in the nuclear magnetic resonance spectrum is 111·8 p.p.m. referred to 85% phosphoric acid.[71–2]

The dielectric constants of pure thiophosphoryl bromide are $\epsilon = 3{\cdot}7$ (solid 18–38°C.) and $\epsilon = 6{\cdot}2$ (liquid 38–48·8°C.),[98] and the dipole moment 1·58 D. whence the moment of the P–S bond is calculated to be 2·00 D.[65]

### CHEMICAL PROPERTIES

Thiophosphoryl bromide reacts readily with ethanol, yet is only slightly attacked by cold water, and may even be steam distilled (with considerable loss).[23] The hydrate of composition $PSBr_3,H_2O$ reported by Michaelis[101] has been shown from its analysis and *X*-ray study to be impure thiophosphoryl bromide. The melting-point diagram of the system $PBr_3/PSBr_3$ shows no evidence of the compound $P_2SBr_6$.[102] It decomposes when heated but in contrast to earlier reports (Mellor, VIII, 1077) only phosphorus tribromide and sulphur are formed.[99] Thiophosphoryl bromide undergoes a ready exchange of sulphur or halogen when heated with certain other phosphoryl or thiophosphoryl halides.[72, 93] Cryoscopic measurements gave no evidence of interaction of thiophosphoryl bromide with tetraphosphorus decasulphide[99] though rearrangement is claimed to occur at higher temperatures.[100]

The action of antimony(III) fluoride on thiophosphoryl bromide yields a mixture of bromofluorides[4] (see page 534). Magnesium reacts with the bromide to give a sulphide $(PS)_n$ of indeterminate structure[103] (see page 419).

## Other Phosphorus Thiobromides

The thiobromides $P_2S_3Br_4$, $P_2SBr$ and $P_2SBr_6$, reported by Michaelis[101] (Mellor, VIII, 1077) have been reinvestigated.[102, 99] The melting-point diagrams of the systems $PBr_3/PSBr_3$ and $P_2S_5/PSBr_3$ show no evidence of the compounds $P_2SBr_6$ or $P_2S_3Br_4$.[102] However, the bromination of tetraphosphorus heptasulphide in cold carbon disulphide yields, besides phosphorus tribromide and thiophosphoryl bromide, two new crystalline thiobromides, diphosphorus hexathiodibromide, $P_2S_6Br_2$, and diphosphorus pentathiotetrabromide, $P_2S_5Br_4$. These are isolated by distilling off the carbon disulphide and taking up the residue in ether. Needle-like crystals of

$P_2S_6Br_2$ separate first, followed more slowly by nodules of $P_2S_5Br_4$. All operations must be carried out in a dry inert atmosphere.

The two thiobromides can be recrystallized unchanged from carbon disulphide, and their molecular weights have been determined ebullioscopically in this solvent. Diphosphorus hexathiodibromide, $P_2S_6Br_2$, has m.p. 118°C. (decomp.), density 1·82 g./c.c., mol. wt. 360 (calc. 414), and diphosphorus pentathiotetrabromide, $P_2S_5Br_4$, m.p. 90°C. (decomp.), density 1·99 g./c.c., mol. wt. 583 (calc. 542). The densities are lower even than those of the phosphorus sulphides (2·03–2·19 g./c.c.) and make an ionic structure improbable. The infra-red spectra show absorptions in the ranges 650–680 cm.$^{-1}$ and 450–520 cm.$^{-1}$, attributed to P=S and P–S–P structures, respectively.

An *X*-ray diffraction study shows that the crystal of $P_2S_6Br_2$ is tetragonal with space group $P\bar{4}2_1c$, $a=b=9{\cdot}79$ A., $c=11{\cdot}51$ A., $D_m=2{\cdot}53$ g./c.c. (flotation), $d_{calc}=2{\cdot}58$ g./c.c. The molecules contain a new type of 6-membered $P_2S_4$ ring with two S–S links (Fig. 1). The ring has a skew 'boat' configuration with P–Br = 2·07, P=S = 1·98, P–S = 2·10 and S–S = 2·03 A.[123]

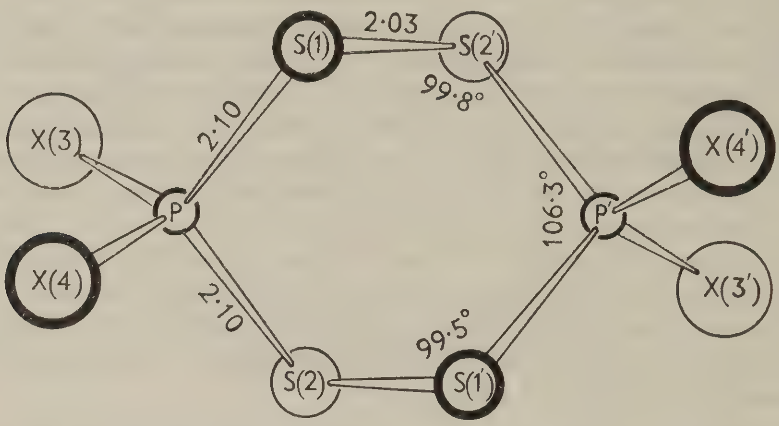


FIG. 1.—The molecule $P_2S_6Br_2$ as it appears in its averaged crystal setting, dimensions of the ring portion being shown. A crystallographic twofold axis relates primed with unprimed atoms. X represents a multiple atomic site ($\frac{1}{2}$Br + $\frac{1}{2}$S)

The thiobromides are decomposed at room temperature by polar solvents, such as acetonitrile, into thiophosphoryl tribromide and an insoluble residue of unknown composition. Thermal decomposition yields the same products together with phosphorus tribromide.[99]

## THIOPHOSPHORYL IODIDES

Thiophosphoryl iodide, $PSI_3$, is made by the slow reaction of phosphorus(III) iodide and sulphur in carbon disulphide at 10–15°C., or from phosphorus, sulphur and iodine (P:S:3I) in the same solvent at 0°C. Both reactions must be carried out in an inert atmosphere, and in the absence of light. In boiling carbon disulphide or benzene the former method yields tetraphosphorus heptasulphide and iodine.

Thiophosphoryl iodide crystallizes from carbon disulphide in brick-red or brownish red leaflets, m.p. 46–48°C. (decomp.). The compound is soluble in carbon disulphide, fairly soluble in aromatic hydrocarbons, carbon tetrachloride, and ether, and dissolves sparingly with decomposition in chloroform, 1,2-dichloroethane and petroleum ether. It is decomposed by light in a few hours at room temperature, with the formation of iodine, phosphorus(III) iodide and tetraphosphorus heptasulphide, but can be kept for longer periods in the dark at −20°C. Moisture also decomposes the compound, forming $H_2S$ and HI.

Raman and infra-red measurements give the characteristic frequencies 309, 321 and 673 cm.$^{-1}$: the symmetry is probably $C_{3v}$.[124]

Of the three phosphorus thioiodides described by Ouvrard and Dreschel (Mellor, VIII, 1079) tetraphosphorus trithiodi-iodide, $P_4S_3I_2$, and diphosphorus thiotetraiodide, $P_2SI_4$, have been confirmed by later workers.[104, 112] The interaction of equi-atomic proportions of phosphorus, sulphur and iodine does not give phosphorus dithiodi-iodide, $P_2S_2I_2$, but a mixture of tetraphosphorus trithiodi-iodide and phosphorus tri-iodide, $PI_3$, together with smaller amounts of tetraphosphorus heptasulphide, $P_4S_7$, red phosphorus and diphosphorus tetraiodide, $P_2I_4$.[104] Diphosphorus thiotetraiodide and diphosphorus dithiotetraiodide, $P_2S_2I_4$, are claimed as products under other conditions.[112] Tetraphosphorus trithiodi-iodide is also formed instead of the dithiodi-iodide by the action of hydrogen sulphide on phosphorus tri-iodide; tetraphosphorus heptasulphide is again a by-product. No reaction occurs between a melt of composition $P_4S_6$ and either iodine or phosphorus tri-iodide, under the mild conditions said by Ouvrard to yield diphosphorus dithiodi-iodide and diphosphorus thiotetraiodide, $P_2SI_4$.

Of the reactions previously claimed to give diphosphorus trithiodi-iodide, the thiohydrolysis of diphosphorus tetraiodide gives a product containing red phosphorus and phosphorus sulphides, while the action of iodine on tetraphosphorus trisulphide yields a mixture of heptasulphide and the trithiodi-iodide. The combination of the elements in the proportions 4P:3S:2I, however, gives an almost quantitative yield of the trithiodi-iodide. After recrystallization from carbon disulphide, the orange-yellow product has m.p. 120·5°C. (decomp.). At the temperature of liquid air it becomes pale yellow.

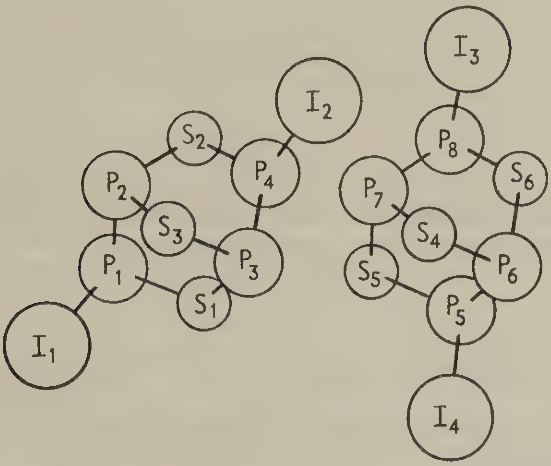


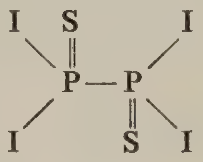
FIG. 2.—The molecular configuration of $P_4S_3I_2$ showing the two enantiomorphous molecules of the asymmetric unit

The structure of tetraphosphorus trithiodi-iodide has been determined by *X*-ray diffraction.[105] The crystals are triclinic with $a = 7{\cdot}31 \pm 0{\cdot}01$, $b = 7{\cdot}35 \pm 0{\cdot}01$, $c = 19{\cdot}61 \pm 0{\cdot}03$ A.; $\alpha = 94°\ 24'$, $\beta = 90°\ 10'$, $\gamma = 90°\ 55'$ (all $\pm 10'$). The observed density is $3{\cdot}0 \pm 0{\cdot}1$ g./c.c. (calculated for 4 molecules/unit cell 3·04 g./c.c.). The molecular structure, a remarkable one, is shown in Fig. 2.

The phosphorus and sulphur atoms are arranged in two 5-membered rings having a common P–S–P angle. In each ring there are two phosphorus atoms bonded together, the two pairs of phosphorus atoms being joined by three sulphur atoms. The iodine atoms, bonded to phosphorus atoms in different rings, are in a *cis* configuration with respect to the $P_4S_3$ skeleton. The average bond lengths are P–I $2{\cdot}48 \pm 0{\cdot}032$ A., P–P $2{\cdot}20 \pm 0{\cdot}04$ A. and P–S $2{\cdot}10 \pm 0{\cdot}04$ A.; the bond angles are S–P–S 105°, P–S–P 104° and P–P–S 102°, 91°. The small value of the last angle, of the type $P_1P_2S_2$, between the two 5-membered rings, gives rise to non-bonded approaches of the type $P_1S_2$ of 3·1 A., 0·6 A. lower than the sum of the van der Waals radii.[106] A further interesting feature of this structure is that the formation of tetraphosphorus trithiodi-iodide from tetraphosphorus trisulphide involves not only the breaking of a P–P bond, but also an exchange of position between phosphorus and sulphur atoms in the $P_4S_3$ molecule.

Little is known of the chemistry of tetraphosphorus trithiodi-iodide. It evolves hydrogen sulphide in moist air, though it is not visibly altered by exposure. Treatment with an excess of iodine decomposes it to tetraphosphorus heptasulphide and phosphorus tri-iodide,[107] a further example of the P–P and P–S bond mobility in such molecules.

A brief communication[112] describes the formation of diphosphorus dithiotetraiodide, $P_2S_2I_4$ (orange-red, m.p. 90–93°C. (decomp.)) and diphosphorus thiotetraiodide, $P_2SI_4$ (brick-red, m.p. 105–110°C. (decomp.)) by interaction of the elements in carbon disulphide with exclusion of light. Both thioiodides decompose on standing with formation of tetraphosphorus heptasulphide, phosphorus iodides and iodine, while with oxygen they yield a polymeric oxyiodide of empirical formula $P_3I_2O_6$. The preparation of diphosphorus dithiotetraiodide (orange, m.p. 93–94°C.) has been repeated, both by the above technique, and by the reaction of diphosphorus tetraiodide with sulphur in carbon disulphide. The preparation, isolation and determination of the melting point and infra-red spectrum, were carried out in the dark under dry helium. The infra-red spectrum was compatible with the structure



and this was confirmed by the $^{31}P$ nuclear magnetic resonance spectrum, which showed a single absorption at $-106$ p.p.m. (85% $H_3PO_4$).[125]

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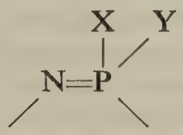
SECTION XVIII

# PHOSPHONITRILIC DERIVATIVES

BY N. L. PADDOCK

Phosphonitrilic derivatives contain the formally unsaturated grouping



The class comprises both linear and cyclic members, and X and Y may be the same or different radicals. Several reviews of phosphonitrilic chemistry are available.[1–6, 158, 170, 185–6, 217] Phosphonitrilic derivatives are so named because complete hydrolysis of the halides gives ammonium phosphate, analogous to the formation of the ammonium salts of organic acids by the hydrolysis of their nitriles. The name is somewhat misleading, however, because monomers containing the P≡N group have not yet been isolated. According to the 1957 IUPAC rules,[7] these substances should be regarded as nitrides, but such a name gives no clue to their structure. They have been more recently described as phosphazenes,[34] which at least implies unsaturation, and recognizes the relation of the series to organic ring systems. The older nomenclature will be used here, as being more widely understood.

## FORMATION OF LINEAR AND CYCLIC SYSTEMS

Some phosphonitrilic chlorides are formed in the reaction with chlorine of phosphorus nitrides[8–9] or thionitride[199] at 800°, and the cyclic trimeric and tetrameric fluorides $(PNF_2)_{3,4}$ can be prepared[10] by the action of nitrogen trifluoride or trifluoromethyl sulphur pentafluoride on the phosphorus nitride, $P_3N_5$, at 700°. The trimeric chloride is also a product of the reaction between sulphur nitride, $S_4N_4$, thionyl chloride and phosphorus trichloride.[11]

The use of azides to prepare phosphonitrilic compounds is comparatively recent.[158] The general reaction is:

$$R_2PX + MN_3 \rightarrow \tfrac{1}{n}(NPR_2)_n + N_2 + MX$$

where X is a halogen and M is an alkali metal, preferably lithium. In published examples R = Br, Ph, Cl,[159, 254] or $CF_3$[160]; the substituents on the phosphorus atom can be different and the method is probably widely applicable. Thus the reaction of sodium azide with a mixture of diphenylchlorophosphine and phenyldichlorophosphine gives an appreciable yield of hexaphenyldichlorophosphonitrile tetramer.[254] Other routes, which have not so far found wide application, include the dehydrofluorination of iminofluorophosphoranes, such as:

$$(Ph_2PF(NH))_n\,^{236} \quad \text{and} \quad (Ph_2PF(NH))_n \xrightarrow[\text{in } Me_2SO]{CsF} (Ph_2PN)_3$$

the pyrolytic decomposition of dimethylhydrazino aryl phosphines, such as:

$$Ph_2PNHN(CH_3)_2,^{255} \qquad Ph_2PNHN(CH_3)_2 \xrightarrow[200°]{\text{Decomp.}} (Ph_2PN)_3$$

or of dialkyldiaminophosphonium chlorides[263]:

$$R_2PNH_2 + NH_2Cl \rightarrow [R_2P(NH_2)_2]Cl \xrightarrow[200^\circ]{\text{Decomp.}} (R_2PN)_3 + NH_4Cl$$

and the reaction of iminobis(aminodiphenylphosphorane) halides with P(V) halides.[281]

The most general method for the preparation of phosphonitrilic derivatives is the ammonolysis of phosphorus pentachloride or its derivatives, the procedure in most cases being based on that devised by Schenck and Römer (Mellor, VIII, 722). Phosphorus pentachloride in an inert solvent is allowed to react with ammonium chloride according to the equation:

$$PCl_5 + NH_4Cl \rightarrow \tfrac{1}{n}(PNCl_2)_n + 4HCl$$

The usual solvent is 1.1.2.2-tetrachloroethane, but carbon tetrachloride, chlorobenzene and *o*-dichlorobenzene can also be used.[12] The product is a mixture of cyclic and linear chlorides,[13] the latter having the general formula $(PNCl_2)_n,PCl_5$. The ratio of the two types of product can be varied by altering the reaction conditions; high yields of the lower cyclic chlorides are obtained by the slow addition of phosphorus pentachloride to a suspension of ammonium chloride in refluxing tetrachloroethane,[13, 15, 17] whereas if an excess of phosphorus pentachloride is used, the product is mainly linear.[13, 17] The highest yields of cyclic trimer ($>70\%$) are obtained if the ammonium chloride is finely divided ($<5\mu$).[256] The reaction is catalyzed by metallic chlorides with acceptor properties,[19] such as ferric, aluminium and magnesium chlorides, or by lithium chloride[232] and also proceeds in the absence of a solvent.[20, 237] or even (in nitrobenzene solution) in the presence of aqueous sodium hydroxide.[257]

The mechanism of the reaction has not been studied in detail. It is probable[2, 17] that ammonium hexachlorophosphate is formed as an intermediate, which breaks down into the unknown trichlorophosphinimine, $PCl_3{:}NH$. Strong indirect evidence to support the production of the first of these intermediates has been produced,[160] and evidence consistent with the hypothesis of phosphinimine formation has been reviewed.[161] In polar solvents at low temperatures phosphorus pentachloride and ammonium chloride react[187, 218] to give a compound $P_3NCl_{12}$, shown by its N.M.R. spectrum to have the structure $[PCl_3{:}N{:}PCl_3]^+PCl_6^-$ (which cation has also been isolated as the tetrachloroborate[228]). The suggested reaction path[188, 282] involves the nucleophilic attack of $NH{:}PCl_3$ on $PCl_4^+$:

$$PCl_4^+PCl_6^- + NH{:}PCl_3 \rightarrow [PCl_3{:}N{:}PCl_3]^+PCl_6^- + HCl$$

At 150° this salt reacts with more $NH{:}PCl_3$ to give[189, 231] another cation,

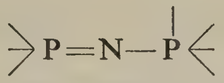
$$[PCl_3{:}N{:}PCl_3]^+ + NH{:}PCl_3 \rightarrow [PCl_3(NPCl_2)_2Cl]^+ + HCl$$

found in solution as its hexachlorophosphate. This latter compound had been previously prepared from sulphur nitride and phosphorus trichloride, or from phosphorus pentachloride and trimeric phosphonitrilic chloride under controlled conditions, and was thought to have the structure $PCl_4^+NPCl_3^-$.[21] The later structure is supported by its electrical conductivity, molecular weight, and especially by its N.M.R. spectrum. The infra-red and Raman spectra of the two compounds have been recorded[289] and an homologous cation with the formula

$$[Cl_3P{-}N{=}P(Cl){-}(N{=}PCl_3)_2]^+$$

has been prepared by the action of phosphorus pentachloride on thiophosphoramide.[249]

An orange bromo-derivative with the empirical formula $P_2NBr_7$ has also been isolated, and is an intermediate in the reaction leading to the formation of the phosphonitrilic bromides.[22] On heating it gives a mixture of small amounts of the trimer and tetramer, and larger quantities of higher homologues. The related compound $C_{24}H_{24}P_2N_3Cl$ (m.p. 245–246·5°) is a principal product[24] of the reaction of ammonia with diphenyl trichlorophosphorane, $Ph_2PCl_3$. While their detailed structures are unknown, it is likely that all these compounds contain the grouping



The phenyl compound gives mainly the cyclic tetrameric phenyl-phosphonitrile on pyrolysis.[24] It is possible that it may be a salt, $[NH_2.PPh_2{:}N.PPh_2.NH_2]^+Cl^-$, like many other phosphonitrilic intermediates.[161]

Ill-defined oily mixtures of linear chlorides of formula $(PNCl_2)_n,PCl_5$, or more probably $[PCl_3(NPCl_2)_{2n}.Cl]^+PCl_6^-$,[161] where $n>1$, can be obtained from the product of incomplete reaction of phosphorus pentachloride and ammonium chloride[12–3] and from the high-temperature reaction of cyclic phosphonitrilic chlorides with phosphorus pentachloride.[25] They are distinguished from the cyclic chlorides by their insolubility in petroleum ether, their ready hydrolysis, their high polarity (dielectric constant about 14) and the ease with which they polymerize to a rubber-like solid in such solvents as refluxing tetrachloroethane.[13] Polymerization in the absence of a solvent is often very slow.

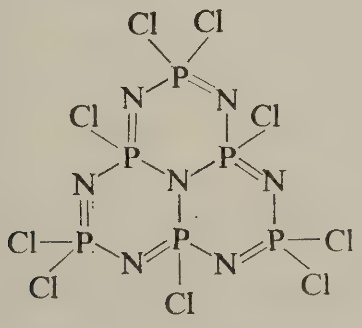
Another series of linear phosphonitrilic derivatives, in which the end-groups are formed from the elements of hydrogen chloride, has been postulated[2, 17] and recognized as a product of the partial ammonolysis of phosphorus pentachloride.[26] The cyclic chlorides may well be formed from this series of derivatives by intramolecular elimination of hydrogen chloride,[161] or from the series previously discussed by the reaction[235]:

$$(PNCl_2)_n.PCl_5 \rightarrow (PNCl_2)_{n-p}.PCl_5 + (PNCl_2)_p$$

The difference between the end-groups of the two series has been demonstrated by nuclear magnetic resonance spectroscopy.[13, 26] Although such linear derivatives are recognized as classes, properly characterized compounds are few; the anilide[12] $P_3N_2Cl_2(NHPh)_7$, the phenyl derivative[27] $Ph(P\,Ph_2N)_3H,HClO_4$ (needles, m.p. 181°) and the fluoride[28] $F(PF_2N)_3H,HF,2H_2O$ (m.p. 32·5°) are known. Other linear derivatives of alkyl and aryl phosphonitriles have also been obtained.[29] Phosphonitrilic chloride chains can be terminated with the elements of other acid chlorides, either by direct addition,[21, 190, 230] or by reaction of hydroxylamine hydrochloride with phosphorus pentachloride[191] and in other ways.[192–3] The compound $PCl_3{:}N.POCl_2$ has been isolated[191–3] and its structure proved by its N.M.R. spectrum.[194]

Cyclic derivatives are better known. The series of cyclic chlorides described by Stokes (Mellor, VIII, 721) has been extended to the octamer, and improved values obtained for their physical properties.[13] The lower members of the series have been separated[30] by vapour-phase chromatography on an analytical scale; their large-scale separation, depending on differences in base strength, has been described in detail.[13, 31] Individual procedures for the confirmed separation of trimer and tetramer chlorides (the most readily formed and commonly used members of the series) have been described.[162, 258]

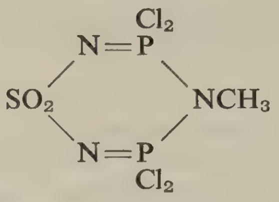
A polycyclic structure



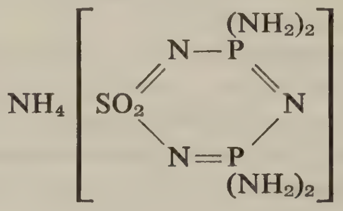
has been proposed[130] for a compound $P_6N_7Cl_9$ which was found by Stokes (*loc. cit.*)[23] with the simple cyclic chlorides. The compound

$$Cl_3P{=}N{-}SO_2{-}N{=}PCl_3$$

obtained by the interaction of phosphorus pentachloride with sulphuryl amide, reacts with heptamethyl disilazane to form a white crystalline derivative, which is formulated[222] as:



and with ammonia to give the analogous salt:



The relation of these to the cyclic phosphonitrilic derivatives is obvious.

The trimeric and tetrameric phosphonitrilic bromides have been prepared from phosphorus pentabromide and ammonium bromide,[22, 33–4] the chief improvement[22, 266] on the original experiments[33] being the maintenance of a comparatively low temperature up to the complete formation of the intermediate $PNBr_2,PBr_5$, or the exclusive use of fractional crystallization in the working-up procedure.[248] In the latter way the pentameric bromide has been isolated. Mixed trimeric chlorobromides have also been obtained[35, 234]; the monobromide pentachloride from phosphorus pentachloride, ammonium bromide and bromine, a dibromide-tetrachloride from phosphorus tribromide, phosphorus pentachloride and excess of ammonium chloride, and a tetrabromide-dichloride from phosphorus trichloride, bromine and ammonium bromide. These compounds together with the trichloride-tribromide are also formed[234] by the reaction of phosphorus pentachloride and ammonium bromide in tetrachloroethane, though there is evidence that the tetrabromide-dichloride of Rice *et al.*[35] is a 1:1 mixture of pentabromide–chloride and tribromide–trichloride.[267] Mixed tetrameric chlorobromides were also detected. The physical properties of the phosphonitrilic halides are given in Tables I–V.

Reaction of ammonium chloride with dimethyl-trichlorophosphorane, followed by treatment with triethylamine, gives the trimeric and tetrameric dimethylphosphonitriles[36]; the base is required for cyclization. The corresponding ethyl derivatives have been prepared[29, 37] by the action of liquid ammonia on diethyltrichlorophosphorane, followed by heating at 220–250°, while dimethyl, diethyl and di-*n*-butyl phosphonitriles are formed by the pyrolysis of the corresponding dialkyldiaminophosphonium chlorides.[263] The lower alkyl phosphonitriles are soluble in water. Similarly, diphenyl-trichlorophosphorane reacts with ammonium chloride, or preferably with ammonia, to give a good yield of tetrameric diphenyl-phosphonitrile and a smaller amount of the trimer.[38] Monophenyl-tetrachlorophosphorane, on ammonolysis, gives three of the four possible stereo-isomers of the tetrameric compound $P_4N_4Cl_4Ph_4$, each phosphorus atom carrying one phenyl group and one chlorine atom.[39, 195] The *cis* (m.p. 191–2°) and *trans* (m.p. 158–9°) isomers of 2,4,6-triphenyl-2,4,6-trichlorotriphosphonitrile[196, 286] can also be isolated under suitable conditions. Analogous bromo-derivatives have been described.[197] For the properties of alkyl and aryl derivatives, see Table VI. Octamethyl tetraphosphonitrile reacts almost quantitatively with molybdenum hexacarbonyl to give a yellow solid,

Table I.—Physical Properties of Phosphonitrilic Halides(a)

| Compound | M.P. (°C.) | $d_4^{20}$ (g.c.c.$^{-1}$) | Crystallographic Data | | | | | P–N stretching frequency(c) (cm.$^{-1}$) | Phosphorus NMR chemical shift(d) (p.p.m.) |
|---|---|---|---|---|---|---|---|---|---|
| | | | Space Group or Cryst. Syst. | Unit Cell Dimensions (A.) | | | $Z$ | | |
| | | | | $a$ | $b$ | $c$ | | | |
| $(PNF_2)_3$ | 27·8[174] | 2·237[42] | $P_{nma}$ or $P_{na}2_1$ | 6·948 | 12·190 | 8·723 | 4[287] | 1297[45, 113] | — |
| $(PNCl_2)_3$ | 112·8 | 1·99[13] | $P_{nma}$ | 14·15<br>14·03 | 12·99<br>12·91 | 6·19<br>6·17 | 4[117]<br>4[118] | 1218[112] | −20 |
| $P_3N_3Cl_5Br$ | 123·5 | 2·27 | Orthorhombic | 14·24 | 6·28 | 13·00 | 4 | 1205[35] | — |
| $P_3N_3Cl_4Br_2$ | 136·5 | 2·44 | $P_{na}2_1$ or $P_{nam}$ | 14·27 | 6·34 | 13·02 | 4 | 1202[35] | — |
| $P_3N_3Cl_3Br_3$ | 142[234] | — | — | — | — | — | — | — | — |
| $P_3N_3Cl_2Br_4$ | 167 | 2·84 | Orthorhombic | 14·29 | 6·48 | 13·33 | 4 | 1180[35] | — |
| $(PNBr_2)_3$ | 191[33] | 3·18 (calc.) | $P_{nam}$ | 14·38 | 6·64 | 13·35 | 4[33] | 1184[58] | — |
| $(PNF_2)_4$ | 30·4 | 2·239[42] | $P_{2_1}/a$ | 7·40<br>7·53 | 13·83<br>$\beta = 109·5°$<br>14·00<br>$\beta = 111·1°$ | 5·16<br>5·15 | 2[127]<br>2[130] | 1419,<br>1439[45, 113] | — |
| $(PNCl_2)_4$(b)(e) | 123·5[13] | 2·18 | $P_{4_2}/n$ | 10·79<br>10·82 | —<br>— | 5·93<br>5·95 | 2[123]<br>2[125] | 1310[112] | +7 |
| $(PNBr_2)_4$ | 202[248] | — | Tetragonal | 11·14 | — | 6·29 | —[33] | 1270 | — |
| $(PNCl_2)_5$ | 41·3[13] | 2·02 | $P_{2_12_12_1}$ | 15·48 | 19·44 | 6·26 | 4[221] | 1355[13] | +17 |
| $(PNBr_2)_5$ | 104·5[248] | 3·08<br>(3·21 calc.) | Triclinic | 10·58 | 9·48 | 14·02 | 2[248] | 1330[248] | — |
| $(PNCl_2)_6$(b) | 92·3[13] | 1·96 | Triclinic | 10·6<br>$\alpha = 93·5°$ | 10·7<br>$\beta = 90°$ | 11·4<br>$\gamma = 117°$ | 2[13] | 1325[13] | +16 |
| $(PNCl_2)_7$ | 8–12[13] | 1·890 | — | — | — | — | — | 1310[13] | +18 |
| $(PNCl_2)_8$ | 57–58[13] | 1·99 | $C_{2/c}$ or $C_c$ | 24·7 | 6·2<br>$\beta = 111°$ | 20·4 | 4 | 1305 | +18 |

The critical temperatures of the lower phosphonitrilic fluorides are $(PNF_2)_3$, 187·7°; $(PNF_2)_4$, 223·2°; $(PNF_2)_5$, 250·8$_{\text{dec.}}$.[287]

(a) Each reference number relates to all data following the previous number in the same row.

(b) See Ref. 13 for other polymorphic forms.

(c) Where all the halogen atoms in a molecule are identical, this refers to an E′ mode in trimeric, Eg mode in tetrameric molecules, to which the P–N stretching motion is an important contributor.[112] If the halogens are mixed, the degeneracy may be lifted and the band may split.

(d) Relative to $H_3PO_4$(85%). Determined by R. F. M. White, and reported in Ref. 13.

(e) For *X*-ray powder diffraction data, see Ref. 126.

Table II.—Optical and Dielectric Properties of Phosphonitrilic Halides

| Property | $(PNF_2)_3$ | $(PNCl_2)_3$ | $(PNBr_2)_3$ | $(PNF_2)_4$ | $(PNCl_2)_4$ | $(PNCl_2)_5$ | $(PNCl_2)_6$ | $(PNCl_2)_7$ |
|---|---|---|---|---|---|---|---|---|
| Refractive Indices[(a)] | $\alpha // c = 1{\cdot}388$<br>$\beta // a = 1{\cdot}419$<br>$\gamma // b = 1{\cdot}443$ | $\alpha // a = 1{\cdot}619$<br>$\beta // c = 1{\cdot}621$<br>$\gamma // b = 1{\cdot}631$ | $\alpha // c = 1{\cdot}720$<br>$\beta // a = 1{\cdot}742$<br>$\gamma // b = 1{\cdot}812$ | $\alpha = 1{\cdot}379$<br>$\beta // b = 1{\cdot}428$<br>$\gamma = 1{\cdot}463$ | $\epsilon = 1{\cdot}675$<br>$\omega = 1{\cdot}678$ | $\alpha = 1{\cdot}629$<br>$\beta = 1{\cdot}644$<br>$\gamma$ undetermined | $\alpha = 1{\cdot}628$<br>$\beta = 1{\cdot}649$<br>$\gamma = 1{\cdot}650$ | —<br>—<br>— |
| $2V$ | 99° | 26° | 54° | 80°<br>$\gamma\hat{}c = 62°$ | | (optically −ve) | 34° | — |
| Dipole Moment[130] ($D$) | — | 0·51 | — | — | 0·39 | 0·47[(b)] | 0·48 | 0·54 |

(a) Optical data for all compounds except the trimeric fluoride[32] obtained by J. K. Leary.[2]
(b) The dielectric constant of the pentameric chloride[13] at 45° is 3·48.

Table III.—Thermodynamic Data for Vaporization of Phosphonitrilic Halides[(a)]

| Compound and State | $A$ | $B$ | B.p. (°C.) | $\Delta H_{\text{subl.}}$ (kcal./mole) | $\Delta H_{\text{vap.}}$ (kcal./mole) | $\Delta H_{\text{fus.}}$ (kcal./mole) | $\Delta S_{\text{vap.}}$ (g.-cal./deg.) |
|---|---|---|---|---|---|---|---|
| $(PNF_2)_3$ (c) | 11·81 | 2806[44] | | 12·8 | 7·68 | 5·12 | 23·7[44] |
| | 11·82 | 2810[42] | | | | | |
| $(PNF_2)_3$ (l) | 8·065 | 1679[44] | 51·8[42] | | | | |
| $(PNCl_2)_3$ (c) | 11·47 | 4171[265] | | 18·2 | 13·2 | 5·0 | 25·0[20] |
| $(PNCl_2)_3$ (l) | 8·357 | 2880[20] | 256·5[14] | | | | |
| $(PNBr_2)_3$ (c) | 11·15 | 5066[265] | | | | | |
| $(PNF_2)_4$ (c) | 11·85 | 3046[44] | | 13·8<br>13·9 | 8·9<br>8·9 | 4·9<br>5·0 | 24·6[42]<br>24·6[44] |
| | 11·76 | 3013[42] | | | | | |
| $(PNF_2)_4$ (l) | 8·247 | 1947[44] | | | | | |
| | 8·26 | 1952[42] | 89·7[42] | | | | |
| $P_4N_4F_6Cl_2$ (l) | 7·923 | 1911 | 105·8 | — | 8·7 | — | 23·1[28] |
| $P_4N_4F_4Cl_4$ (l) | 7·615 | 1911 | 130·5 | — | 8·7 | — | 21·7[40] |
| $(PNCl_2)_4$ (c) | 13·79 | 5593[265] | | | | | |
| $(PNCl_2)_4$ (l) | 8·498 | 3358 | 328·5 | 23·1 | 15·35[238] | 7·60[16] | 25·7[14] |
| $(PNCl_2)_5$ | 9·10 | 3973 | 371·5 | — | 18·15[238] | — | — |
| $(PNCl_2)_6$ | 9·576 | 4533 | — | — | 20·7[238] | — | — |
| $(PNCl_2)_7$ | 10 | 5060 | — | — | 23·1[238] | — | — |

[(a)] $A$ and $B$ are constants in the vapour-pressure formula $\log_{10} p(\text{mm. Hg}) = A - B/T$, where $T$ is the absolute temperature. Post-scripts (c), (l), stand for crystal, liquid, respectively.

*Table IV.—Physical Properties of Liquid Phosphonitrilic Fluorides*[45]

| Property | $(PNF_2)_5$ | $(PNF_2)_6$ | $(PNF_2)_7$ | $(PNF_2)_8$ | $(PNF_2)_9$ | $(PNF_2)_{10}$ | $(PNF_2)_{11}$ |
|---|---|---|---|---|---|---|---|
| M.p. (°C.) | −50 | −45·5 | −61 | −16·9 | < −78 | −51 | < −78 |
| B.p.(b) (°C.) | 120·1 | 147·2 | 170·7 | 192·8 | 214·4 | 230·8 | 246·7 |
| $\Delta H_{vap.}$ (kcal./mole) | 9·8 | (a) | 11·6 | 12·0 | 12·7 | 13·5 | 14·6 |
| $\Delta S_{vap.}$ (g.-cal./deg/mole) | 24·9 | (a) | 26·2 | 25·8 | 26·1 | 26·9 | 28·0 |
| $d_4^{20}$ (g. c.c.$^{-1}$) | 1·8259 | 1·8410(d) | 1·8496 | 1·8567 | 1·8589(e) | 1·8638 | 1·8644 |
| $n_{4538}^{20}$ | 1·3550 | 1·3604 | 1·3644 | 1·3677 | 1·3699 | 1·3710 | 1·3723 |
| $n_D^{20}$ | 1·3482 | 1·3533 | 1·3570 | 1·3602 | 1·3622 | 1·3633 | 1·3645 |
| P–N stretching frequency(c) (cm.$^{-1}$) | 1439 | 1408 | 1400 | 1386 | 1375 | 1363 | 1357 |

(a) Not calculated; v.p. data inaccurate.

(b) For higher polymers, approx. b.ps. at 12·65 mm. are: $(PNF_2)_{12}$, 143–148°; $(PNF_2)_{13}$, 154–159°; $(PNF_2)_{14}$, 166–170°.

(c) The most intense band in the i.r. spectrum, corresponding to E′ and Eg modes in the trimer and tetramer, respectively.[112–3]

(d) Temperature coefficient of density $-2{\cdot}76 \times 10^{-3}$ g. c.c.$^{-1}$ deg.$^{-1}$ over the range 20–80°.

(e) Temperature coefficient of density $-2{\cdot}10 \times 10^{-3}$ g. c.c.$^{-1}$ deg.$^{-1}$ over the range 10–60°.

$N_4P_4Me_8,Mo(CO)_4$, stable in air, but oxidized in solution. The infra-red spectrum is consistent with $C_{2v}$ symmetry, with the phosphonitrile occupying two *cis*-positions of the molybdenum octahedron.[219]

*Table VI.—Properties of Alkyl- and Aryl-Phosphonitriles*

| Compound | M.p. (°C.) | P–N stretching frequency (cm.$^{-1}$) |
|---|---|---|
| $P_3N_3Me_6$ | 195–196 | 1180[36] |
| $P_3N_3Me_3Cl_3$ | 156–157 | 1190[79] |
| $P_3N_3Et_6$ | 117·5–119 | 1157[37] |
| $P_3N_3nBu_6$ | 45–50 | 1155[263] |
| $P_3N_3Ph_6$ | 232[78] | 1190[37] |
| $P_3N_3Ph_2Cl_4$(d) | 92·5[27] | — |
| $P_4N_4Me_8$ | 163–164 | 1220[36] |
| $P_4N_4Et_8$ | liquid | 1231, 1280[37] |
| $P_4N_4Ph_8$(a) | (I) 230, (II) 310[80] (a)<br>319·5–321[38] | 1213[37] |
| $P_4N_4Ph_4Cl_4$(I)(b) | 176[80] | — |
| $P_4N_4Ph_4Cl_4$(II)(b) | 205[80] | — |
| $P_4N_4Ph_4Cl_4$(III)(c) | 248 | 1313, 1294, 1282[39] |
| $P_4N_4Ph_4Cl_4$(IV)(c) | 148 | 1308, 1292, 1275[39] |

(a) (I) and (II) may be configurational isomers. Only the higher-melting form has been found in later work.[38]

(b) (I) and (II) are position isomers. Two phosphorus atoms carry two phenyl groups each.

(c) (III) and (IV) are stereo-isomers. Each phosphorus atom carries a phenyl group and a chlorine atom.

(d) For derivatives, see Table VIII.

## SUBSTITUTION AND ADDITION REACTIONS OF THE PHOSPHONITRILIC CHLORIDES

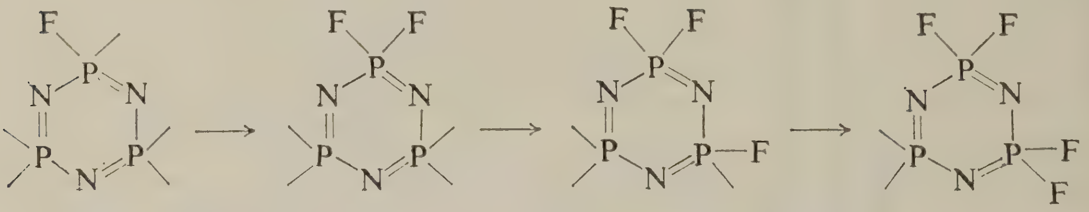
Most cyclic derivatives have been prepared by substitution reactions from the chlorides. The majority of the reactions appear to be nucleophilic displacements. The simplest group of such reactions is that in which chlorine is replaced by fluorine or by a pseudo-halogen group, if we except the exchange process of radioactive chloride ion and the homologous chlorophosphonitriles $(NPCl_2)_{3-6}$, in acetonitrile solution, which was shown[229] to be of second order. The order of reactivity in this case was shown to be $(PNCl_2)_4 > (PNCl_2)_5 > (PNCl_2)_6 > (PNCl_2)_3$.

*Table V.—Solubilities of Phosphonitrilic Chlorides in Organic Solvents*

| Compound | Dioxan | Diethyl ether | Xylene | Toluene | Benzene | *s*-Tetra-chloro-ethane | Carbon tetra-chloride | Carbon disulphide | *n*-Heptane | *n*-Hexane | *n*-Pentane | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(PNCl_2)_3$ | | 46·5 | | | 57·4 | | | | | | | 18 |
| | 29·55 | 46·4 | 38·8 | 47·3 | 55·0 | | 38·9 | 52·05 | 27·9(b) | | | 64 |
| | | | | | 56·5 | 33·4 | 38·3 | | | 25·5 | 25·5 | (a) |
| $(PNCl_2)_4$ | | 12·3 | | | 20·9 | | | | | | | 18 |
| | 8·2 | 12·4 | 13·9 | 17·8 | 21·4 | | 16·6 | 22·0 | 8·4(b) | | | 64 |
| | | | | | 23·5 | 7·9 | 15·5 | | | 7·0 | 6·1 | (a) |
| $(PNCl_2)_5$ | | | | | | | | | 1030 | | ~2000 | (a) |
| $(PNCl_2)_6$ | | | | | 145 | | 98 | | | 34 | 27·8 | (a) |

(a) L. G. Lund, reported in Ref. 2.
(b) 80–90° petrol.

Fluorination of the trimeric chloride with lead fluoride leads to the tetrameric chlorofluorides[28] $P_4N_4Cl_2F_6$ and[40] $P_4N_4Cl_4F_4$; both compounds polymerize on heating, and depolymerize at higher temperatures, with the formation[40] of the trimeric chloride–fluorides $P_3N_3Cl_2F_4$ and $P_3N_3Cl_4F_2$. The simple trimeric and tetrameric fluorides have been obtained by the action of potassium fluorosulphite, $KSO_2F$, on the corresponding chlorides[41–2]; the trimeric chloride had evidently been obtained in earlier work, but was not then recognized.[43] The orientation of the substituents in these reactions has been established by infra-red and N.M.R. spectroscopy, and geminal substitution[163–5] takes place almost exclusively,



though one of two trimeric fluoride chlorides described some years ago[40] does not fall into this pattern. It therefore seems that redistribution reactions may occur at high temperatures.

Potassium fluorosulphite in the above preparation can be replaced by a mixture of sulphur dioxide and potassium fluoride,[44–5] which reacts readily with a mixture of the cyclic chlorides at 100–110°C.[45] The existence of a series of cyclic polymers up to at least $(PNF_2)_{17}$ has been demonstrated.[45] Acetonitrile[204] and nitrobenzene[205] are suitable media for the reaction with simple fluorides, which is catalyzed by water and hydrogen fluorides.[205] Silver fluoride has also been used[46]; see also Ref. 10 for a preparation from a phosphorus nitride, and Tables I–IV for the properties of the phosphonitrilic fluorides and chloride–fluorides.

The phosphonitrilic fluorides are all very volatile, resembling the *n*-fluoroparaffins in this respect, and in their poor and anomalous solvent properties; for example the pentameric fluoride is immiscible with ethyl iodide at room temperature. The phosphonitrilic fluorides differ from the fluoroparaffins in being very flexible molecules, the liquids having both low viscosities and low temperature-coefficients of viscosity. The viscosity of the pentameric fluoride, $(PNF_2)_5$, is given by

$$\log_{10} \eta(\text{centipoises}) = 556/T - 1{\cdot}728$$

over the range $t = 20$–$80$°C. Its activation energy for viscous flow is 2·54 kcal. mole$^{-1}$, and that of the nonameric fluoride is 2·75 kcal. mole$^{-1}$. The molar volumes of the series can be expressed by the equation $V_m = 43{\cdot}753n + 8{\cdot}19$ c.c., with an average deviation of 0·27 c.c., and the molar refractivities by $[M]_D = 10{\cdot}103n - 1{\cdot}86$ c.c., with an average deviation of 0·06 c.c., where $n$ is the degree of polymerization.[45]

The trimeric phosphonitrilic azide $P_3N_3(N_3)_6$ has been prepared[47] from sodium azide and the trimeric chloride, and the amide–azide $P_3N_3(NH_2)_2(N_3)_4$ (white needles, m.p. 81–82°) from the diamide-tetrachloride.[48] The trimeric[49] and tetrameric[50] *iso*thiocyanates have been prepared similarly. The trimer (white crystals) melts at 41–42°, is very soluble in carbon tetrachloride and is insoluble in water. 100 g. of ether, *n*-heptane and acetone dissolve 20·9 g., 5·23 g. and 5·14 g. of the trimer, respectively. The solubilities of the tetramer in 100 g. of each of the four solvents, carbon tetrachloride, ether, *n*-heptane and acetone are 11·2 g., 0·7 g., 0·26 g. and 0·1 g. It is insoluble in water. The infra-red spectra of the thiocyanates show that the ring-systems are retained. The *iso*thiocyanate group reacts normally with amino-, hydroxy- and hydrazino-compounds. (For m.p. of derivatives, see Tables VII, VIII.)

The *iso*cyanate group cannot be introduced so simply, but an aminotetrachloro-*iso*cyanato triphosphonitrile has been prepared by the action of carbonyl chloride on 1,3-diaminotetrachloro-triphosphonitrile in chlorobenzene. The compound, m.p.

105°C., showed infra-red absorption bands at 3290 cm.$^{-1}$ ($-NH_2$), 2275 cm.$^{-1}$ ($-NCO$) and 1210 cm.$^{-1}$ (P–N ring stretch), and was converted to the corresponding ethyl urethane, m.p. 132°C.[261]

*Table VII.—Melting-points of Phosphonitrilamides* $P_3N_3R_6$

| R. | M.p. (°C.) | Ref. | R. | M.p. (°C.) | Ref. |
|---|---|---|---|---|---|
| MeNH | 258 | 71 | PhNH | 264 | 68 |
| $Me_2N$ | 100 | 71 | $p$-$CH_3.C_6H_4NH$ | 242 | 70 |
| $(CH_2)_2N$ | 147·5 | 73 | $NH_2.C(S).NH$(b) | 190 | 50 |
| $NH.NH_2$(a) | >360 | 74 | Bu.NH.C(S)NH | 155 | 50 |
| EtNH | 119 | 72 | Ph.NH.C(S)NH | 151 | 50 |
| $C_6H_{11}NH$ | 166 | 72 | EtO.C(S)NH | 174 | 50 |
| $C_5H_{10}N$ | 266 | 70 | PhNH.NH.C(S)NH | 165 | 50 |

(a) Benzaldehyde derivative m.p. 250° (decomp.); salicylaldehyde derivative m.p. 225° (decomp.).

(b) This, and the following four compounds, are derivatives of the thiocyanate.[50]

*Table VIII.—Melting-points of Mixed Trimeric Phosphonitrilic Derivatives*

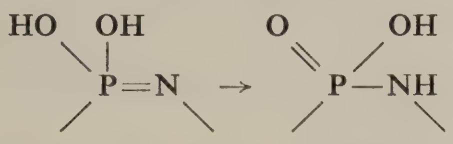
| Compound | M.p. (°C.) | Ref. | Compound | M.p. (°C.) | Ref. |
|---|---|---|---|---|---|
| $P_3N_3Cl_4(NH_2)_2$ | 162 (dec.) | 64 | $P_3N_3Cl_2Ph_2(NHPh)_2$ | 193 | 70 |
| $P_3N_3Cl_4(NHMe)_2$ | 98 | 70 | $P_3N_3Ph_2(NHPh)_4$ | 256–257 | 70 |
| $P_3N_3Cl_4(NEt_2)_2$ | 134 | 72 | $P_3N_3Ph_2(NH_2)_2(NHPh)_2$ | 218 | 70 |
| $P_3N_3Cl_4(NC_6H_{11})_2$ | 200 | 72 | $P_3N_3Ph_2(NH_2)_4$(a) | 106, 275 | 81 |
| $P_3N_3Cl_3(NMe_2)_3$ | 107 | 71 | $P_3N_3Ph_2(NHMe)_4$ | 174 | 81 |
| $P_3N_3Cl_3(NEt_2)_3$ | 162 | 69 | $P_3N_3Ph_2(NMe_2)_4$ | 120 | 81 |
| $P_3N_3Cl_2(NHPh)_4$ | 191 | 70 | $P_3N_3Ph_2(NH_2)_2(NHMe)_2$ | 140 | 81 |
| $P_3N_3Cl_2(p\text{-}NHC_6H_4.CH_3)_4$ | 174 | 70 | $P_3N_3Ph_2(NH_2)_2(NMe_2)_2$ | 137 | 81 |
| $P_3N_3Cl_2Ph_2(NH_2)_2$ | 162–163 | 70, 81 | | | |

(a) Two modifications.

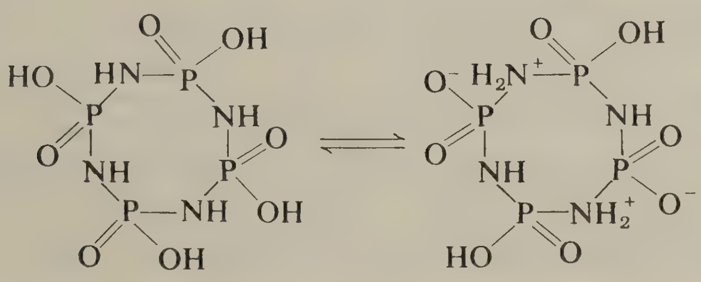
For further data see reference 264.

## Hydrolysis

The phosphonitrilic chlorides can be hydrolyzed to the corresponding acids, though slowly. Kinetic data for hydrolysis and other electrophilic substitution reactions of phosphonitrilic chlorides have been assembled and discussed.[161, 275] In general, the phosphonitrilic acids rearrange to the tautomeric metaphosphimic acids which have one replaceable hydrogen atom in each repeating unit[203]:



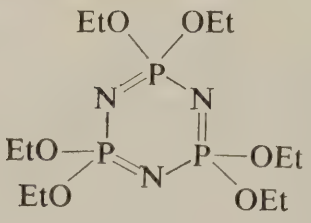
Exceptionally, the tetrameric acid is dibasic on rapid and tetrabasic on slow titration[53] suggesting a slow equilibration of the normal and zwitterionic structures:



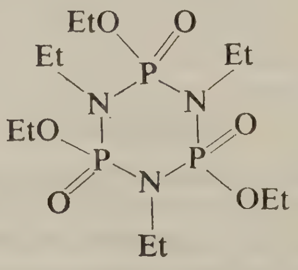
The acid is normally isolated as the dihydrate; it is orthorhombic[54] space group $P_{2_1 2_1 2}$, $Z=2$. The eight-membered rings have at least a two-fold axis of symmetry. The di-potassium and di-rubidium salts are isomorphous with the acid, in which the water molecules are presumably present as $H_3O^+$ cations. The cell constants are given below. The diammonium salt has a similar structure.[54]

| | *a* (A.) | *b* (A.) | *c* (A.) |
|---|---|---|---|
| $P_4N_4(OH)_8,2H_2O$ | 13·92 | 8·34 | 5·05 |
| $P_4N_4(OH)_6(OK)_2$ | 13·89 | 8·07 | 5·03 |
| $P_4N_4(OH)_6(ORb)_2$ | 14·03 | 8·24 | 5·06 |

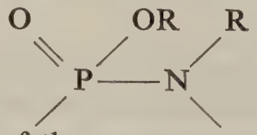
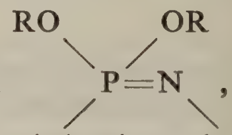
The preparation of the sodium and potassium salts of triphosphonitrilic acid has also been described.[51] The infra-red spectra of a number of salts of the trimeric and tetrameric acids have been reported.[52] The salts react with sodium hypochlorite to give N-chlorophosphonitrilates,[55] with oxidizing properties like organic N-chloro compounds. The materials contain up to 45% of available chlorine and are said to be readily and completely soluble in water. The same type of isomerism occurs in the phosphonitrilic esters.[56] The normal ester



is a colourless oil, soluble in water. The isomeric compound



prepared from the trisilver salt of trimetaphosphimic acid and silver iodide,[56] is crystalline (m.p. 74·5°) and forms a di-hydrochloride. The similarly prepared tetraethyl ester of the tetrameric N-ethyl acid is a yellowish oil. The singly-bonded trimeric ring system is broken down to linear derivatives in alkali.[56]

The grouping  is evidently more stable than  ,

mainly because of the great strength of the phosphoryl bond, and the thermal rearrangement of O-alkyl to N-alkyl esters has been demonstrated. It is catalyzed by alkyl halides.[262] The trimeric[57] (b.p. 127°/0·03 mm.) and tetrameric[58] dimethoxyphosphonitriles $P_3N_3(OMe)_6$ and $P_4N_4(OMe)_8$ have also been obtained. Other trimeric alkoxides,[57, 59, 61, 166, 276–7] phenoxides,[60, 245, 259] mercaptides[61, 198] and nitroxyalkyl esters[167] have been described, as have the pentameric, hexameric, heptameric, and octameric dimethoxy and diphenoxy phosphonitriles.[252] Several polyfluoroalkyl phosphonitrilates have been prepared by the action of the alkali-metal salts of polyfluorocarbinols on the chlorides.[62, 252] They are converted to chloro-fluoro-compounds by chlorination in carbon tetrachloride solution in ultra-violet light,[63] but have otherwise extraordinary chemical and thermal stability; they can be distilled at 500°C. without decomposition, and are only slowly attacked by hot acid or alkali. For their physical properties, see Table IX.

*Table IX.—Physical Properties of Fluoroalkyl Phosphonitrilates,*(a) $[PN(OR)_2]_{3,\,4}$

| Trimeric Esters | | | Tetrameric Esters | | |
|---|---|---|---|---|---|
| R. | M.p. (°C.) | B.p. | R. | M.p. (°C.) | B.p. |
| $CH_2CF_3$ | 38 | 248°/743 mm.<br>115–116°/3 mm. | $CH_2CF_3$ | 65 | 139–140°/3 mm. |
| $CH_2(CF_2)_2F$(b) | 16–18 | 136·5°/6 mm. | $CH_2(CF_2)_2F$(d) | — | 142–144°/3 mm. |
| $CH_2(CF_2)_3F$(c) | — | 154°/3 mm. | $CH_2(CF_2)_3F$ | 84–85 | 305°/743 mm.<br>168·5–171·5°/3 mm. |
| $CH_2(CF_2)_6H$ | 32–36 | 258–260°/2 mm. | $CH_2(CF_2)_6H$ | — | 398–401°/750 mm.<br>265°/1 mm. |
| $CH_2(CF_2)_{10}H$ | 103–105 | 320–324°/2 mm. | $CH_2(CF_2)_{10}H$ | 102–105 | 312–320°/0·1 mm. |
| $CCl_2(CF_2)_2F$ | 147–148 | — | $CCl_2(CF_2)_3F$ | 129–132 | — |
| $CCl_2(CF_2)_3F$ | 94 | — | $CCl_2(CF_2)_{10}Cl$ | 145–150 | — |

(a) Data for chloro-fluoro esters from Ref. 63; otherwise Ref. 62.
(b) $n_D^{28}=1{\cdot}3365$.
(c) $n_D^{25}=1{\cdot}3309$.
(d) $n_D^{27}=1{\cdot}353$.

## Ammonolysis

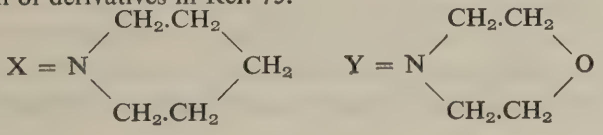
Ammonia and amines also react with the phosphonitrilic chlorides, the main product from the trimer being the diamide-tetrachloride.[64] Complete ammonolysis is difficult, but can be achieved in liquid ammonia at room temperature within 48 hr.[65] Ammonolysis of the tetrameric chloride gives the diamide hexachloride and the tetra-amide tetrachloride[64, 66]; again, the fully-substituted amido-derivative is formed in liquid ammonia.[65] On heating, both trimeric and tetrameric phosphonitrilamides evolve ammonia, the eventual product being phospham, of empirical composition (PN:NH); its infra-red spectrum[67, 201–2] suggests that the typical phosphonitrilic bond is retained. In the presence of suitable impurities, triphosphonitrilic hexamide gives a friable polymeric foam.[246]

Substitution of the chlorine atoms by primary and secondary amine residues occurs comparatively readily, and such derivatives are numerous. Melting points of trimeric derivatives are given in Tables VII and VIII, and of tetrameric derivatives in Table X.

*Table X.—Melting-points of Tetrameric Phosphonitrilamides*

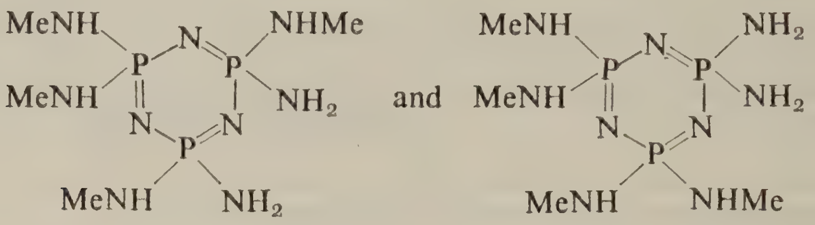
| Compound | M.p. (°C.) | Ref. | Compound | M.p. (°C.) | Ref. |
|---|---|---|---|---|---|
| $P_4N_4(NMe_2)_8$ | 237 | 72 | $P_4N_4Cl_6(NHMe)_2$ | 143 | 75(b) |
| $P_4N_4[N(CH_2)_2]_8$ | 262 (dec.) | 73 | $P_4N_4Cl_6(NMe_2)_2$ | 171 (subl.) | 75 |
| $P_4N_4(NH.Ph)_8$ | 244 | 68 | $P_4N_4Cl_6(NHEt)_2$ | 113 (subl.) | 75 |
| $P_4N_4[NH.C(S)NH_2]_8$ | 120 (dec.) | 50(a) | $P_4N_4Cl_6(NH.CMe_2)_2$ | 124 | 75 |
| $P_4N_4[NH.C(S)NHBu]_8$ | 105 | 50 | $P_4N_4Cl_6(NHPh)_2$ | 166 | 75 |
| $P_4N_4[NH.C(S)NHPh]_8$ | 139 | 50 | $P_4N_4Cl_6(NMePh)_2$ | 146 | 75 |
| $P_4N_4[NH.C(S)OEt]_8$ | 189 | 50 | $P_4N_4Cl_6(o\text{-Tol.})_2$ | 172 | 75 |
| $P_4N_4[NH.C(S)NH.NHPh]_8$ | 153 (dec.) | 50 | $P_4N_4Cl_6(m\text{-Tol.})_2$ | 204 | 75 |
| $P_4N_4Cl_6(NH_2)_2$ | 217–218 | 66 | $P_4N_4Cl_6(p\text{-Tol.})_2$ | 196 | 75 |
| $P_4N_4Cl_4(NH_2)_4$ | 161–162 | 66 | $P_4N_4Cl_6X_2$(c) | 194 | 75 |
| | | | $P_4N_4Cl_6Y_2$(c) | 205 | 75 |

(a) All compounds reported in Ref. 50 are derivatives of the thiocyanate.
(b) See text for orientation of derivatives in Ref. 75.
(c)

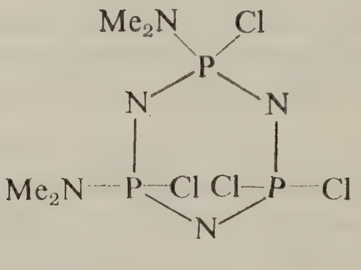


The trimeric tetrachloride-bis(ethylene-diamide)[70] and similar derivatives of aromatic diamines have also been prepared.[70] Charge-transfer type complexes between phosphonitrilic chlorides and phosphonitrilic amides have been described.[214] The dipole moments of a number of phosphonitrilic amides have been measured.[215]

Most mixed derivatives contain an even number of each constituent, as may be seen from Tables VIII and X. It has therefore often been supposed that the chlorine atoms in the phosphonitrilic chlorides are substituted in pairs. This is not always so. It has been shown[71] that in the trimeric tetrachloride bis-dimethylamide, the two amine groups are attached to different phosphorus atoms, since further reaction with dimethylamine gives a tris-dimethylamide in which all the phosphorus atoms are equivalent (NMR). By a combination of chemical and spectroscopic evidence, the orientations of several mixed trimeric amide derivatives have been worked out,[71] and the following pair of isomers recognized.



The mechanism of these substitution reactions is not yet known. They appear to be nucleophilic substitutions, and it is therefore not surprising that the attachment of an amido-group, capable of feeding electrons back to phosphorus, should discourage further attack at the same centre. It is consistent with this view that the NMR spectra of disubstituted aminolysis products of tetrameric phosphonitrilic chloride show that the amine groups occupy positions remote from each other.[75, 200] In the case of the bis-dimethylamido derivative made from the trimeric chloride and dimethylamine, both amido substituents, while being on different phosphorus atoms, lie on the same side of the ring.[168, 244] *Cis-trans* isomerization of these and other dialkylamido derivatives occurs in the presence of aluminium chloride[241] or substituted ammonium chlorides.[242]



However, geminal substitution by amines can occur[251] and has been established for partial substitution for ethylene imine.[169] Fully substituted trimeric and tetrameric amidophosphonitriles prepared by the action of ammonia or amines on the chlorides are numerous and have been listed,[170, 243–4, 252] as have derivatives with only a single alkylamino group.[284]

Orientational effects have been interpreted in terms of base strength,[71] and it is noteworthy that the phosphorus atom is strongly electrophilic. Trimethylamine reacts readily with triphosphonitrilic chloride, with evolution of methyl chloride and partial replacement of the chlorine atoms by dimethylamido-groups.[77] The importance of steric effects in substitution reactions has also been recognized.[76] The reaction of trimeric phosphonitrilic chloride with piperidine in toluene at 0° follows a mixed second and third order rate law, and is catalyzed by tri-*n*-butylamine.[239] The aminolysis of phosphonitrilic fluorides, chlorides, and bromides by propylamine in acetonitrile is also of second order, the reactivity of the halides being in the order $(PNBr_2)_4 > (PNBr_2)_3 \sim (PNCl_2)_4 > (PNCl_2)_3 \sim (PNF_2)_4 > (PNF_2)_3$.[283]

### Reactions with Grignard Reagents

The phosphonitrilic chlorides also undergo substitution reactions with Grignard reagents; hexaphenyl triphosphonitrile has been obtained in small yield from phenyl magnesium bromide and the trimeric chloride.[27, 78] Alkyl magnesium halides react with all three chlorine atoms of tris-dimethylamido-trichloro-triphosphonitrile; the amine groups were removed subsequently with anhydrous hydrogen chloride.[79] With phenyl magnesium bromide, the tetrameric chloride gave[80] two tetraphenyl derivatives, in which degradative experiments showed the phenyl groups to be present in pairs. Two octaphenyl derivatives were also isolated: later workers[216] have claimed that these are 2,2,6,6-tetraphenyl-4,4,8,8-tetrachloro-tetraphosphonitrile (m.p. 212·5°) and 2,2,4,4-tetrachloro-6-phenyl-6-triphenyl phosphinimino triphosphonitrile (m.p. 181°), formed by ring contraction. Similar triphenyl-phosphinimino derivatives can be formed by the action of triphenyldibromophosphorane on aminophosphonitriles.[272]

### Friedel–Crafts Reaction

The trimeric chloride also undergoes the Friedel–Crafts reaction with benzene and aluminium chloride, with the formation of diphenyl-tetrachloro-triphosphonitrile.[27] Several compounds have been prepared from this by reaction with ammonia or amines; for m.p., see Table VIII and Ref. 279. Further phenylation of the diphenyl-tetrachloro compound under more rigorous conditions gives the 2,2,4,4-tetraphenyl and 2,2,4,4,6,6-hexaphenyl derivatives. Toluene and chlorobenzene react similarly, but other aromatic hydrocarbons give no products which can be isolated.[280] Similarly the reaction of *trans*-2,4,6-trichloro-2,4,6-triphenyltriphosphonitrile[283] with benzene and aluminium chloride can be made to give good yields of the 2,4-dichloro-2,4,6,6-tetraphenyl- or 2-chloro-2,4,4,6,6-pentaphenyl derivatives.[264] Part of the chlorine in the trimeric and tetrameric chlorides can be replaced by radicals, formed by the action of ultra-violet light on solutions of the chlorides in benzene and in decahydronaphthalene.[82] Butoxy-phosphonitriles have been obtained, probably in a highly polymeric form, by the action of high-energy electrons (0·6 Mev.) on a solution of the tetrameric chloride in butanol.[83] The reaction of phosphonitrilic halides with sodium in liquid ammonia can be used in the quantitative determination of the halogen.[84] Trimeric phosphonitrilic chloride also undergoes a remarkable reaction with sodium benzoate, and with the salts of other organic acids, to give benzonitrile or its equivalent. It is suggested that the normal benzoate which is formed first undergoes a tautomeric change to an N-benzoyl compound.[85] Exchange of oxygen and nitrogen then occurs, by a mechanism which may be similar to that of the replacement of nitrogen by oxygen in the hydrolysis of the trimeta-phosphimate ion.[86] The phosphonitrilic esters undergo a similar reaction, giving ethyl chloride, ethyl phosphenate and 2,4,6-triphenyl-1,3,5-triazine.[250] Trimeric phosphonitrilic chloride also reacts with silver trifluoro-acetate, with the formation of trifluoro-acetonitrile.[87]

The reactions of phosphonitrilic derivatives with electron acceptors have been less studied. The trimeric and tetrameric chlorides are sufficiently basic to take up one

Number of protons taken up by the phosphonitrilic chlorides $(NPCl_2)_n$ in 100% sulphuric acid[161]

| $n$ | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|
| No. of protons (cryoscopic) | 1·2 | 2·0 | 2·0 | 2·0 | 2·3 | 2·8 |
| No. of protons (conductimetric) | 1·14 | 1·72 | 2·20 | 2·63 | 2·20 | 2·60 |

and two protons respectively[70] to give the compounds $(PNCl_2)_3,HClO_4$ and $(PNCl_2)_4,2HClO_4$, which can be recrystallized from acetic acid containing perchloric acid. They explode on heating. A comparable result was obtained by cryoscopy in sulphuric acid[2]; the pentameric and hexameric chlorides also take up two protons each.

The trimeric chloride is the strongest base of the series,[2] and is comparable in this respect with benzoic acid. Electron release to phosphorus, especially by amido-groups, increases the base strength considerably. In nitrobenzene, the amidophosphonitriles are stronger bases than the parent amine[209]: the relative base strengths in nitrobenzene are a good measure of proton-accepting capacity.[210] There is good evidence[209, 211] that protonation takes place on the ring, rather than in exocyclic positions. Ethylphosphonitriles are also quite strongly basic:

Base strengths of trimeric and tetrameric phosphonitrilic derivatives[161, 210–1]

| R | Cl | Et | $CF_3$ | Ph | $P–Cl–C_6H_4$ |
|---|---|---|---|---|---|
| $pKa(NPR_2)_3$ | −8·2[161] | 6·4, 5·9(a) | <6·0 | 1·5 | −1·4 |
| $pKa(NPR_2)_4$ | −8·6[161] | 7·6, 6·5(a) | — | 2·2 | — |

| R | $NH_2$ | NHMe | NHEt | $NHPr^n$ | $NHPr^i$ | $NHBu^n$ |
|---|---|---|---|---|---|---|
| $pKa(NPR_2)_3$ | 7·65(a) | 8·8 | 8·2, 8·67(a) | 7·9 | 8·4 | 7·9 |
| $pKa(NPR_2)_4$ | 7·55(a) | 8·2 | 8·1, 8·70(a) | 8·3 | 8·1 | 7·6 |

| R | $NHBu^i$ | $NHBu^t$ | *cyclo*-hexylamino | piperidino | $NMe_2$ | $NEt_2$ |
|---|---|---|---|---|---|---|
| $pKa(NPR_2)_3$ | — | 8·0 | 7·9 | 8·4 | 7·6 | 8·5 |
| $pKa(NPR_2)_4$ | 8·0 | 8·8 | — | 8·4 | 8·3 | 8·3 |

| R | OMe | OEt | $OPr^i$ | $OBu^n$ | $OCH_2Ph$ | $OCH_2CF_3$ | OPh |
|---|---|---|---|---|---|---|---|
| $pKa(NPR_2)_3$ | −1·9 | −0·2 | 1·4 | 0·1 | −2·1 | <−6·0 | −5·8 |
| $pKa(NPR_2)_4$ | −1·0 | 0·6 | 2·1 | 0·7 | −1·6 | <−6·0 | −6·0 |

| R | $O–C_6H_4–pOMe$ | $\beta OC_{10}H_7$ | SEt | $SPr^n$ | $SC_6H_{11}$ | $SCH_2Ph$ | SPh |
|---|---|---|---|---|---|---|---|
| $pKa(NPR_2)_3$ | −5·4 | <−6·0 | −2·8 | −2·6 | −2·2 | −4·2 | −4·8 |
| $pKa(NPR_2)_4$ | −5·2 | <−6·0 | | | | | |

(All measurements in nitrobenzene solution except (*a*) in water.)

Further study of the homologous series of phosphonitrilic chlorides shows an interesting alternation both of basicity and of ionization potential, consistent with the modulation of the main $\pi$-system by weaker Hückel-type interactions in the $\pi'$ in-plane system.[220]

Base strengths and ionization potentials of phosphonitrilic chlorides $(NPCl_2)_n$

| $n$ | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|
| $\Delta pK$ | 0 | 0·10 | 0·28 | 0·08 | 0·18 | 0·14 |
| Ionization potential | 10·26 | 9·80 | 9·83 | 9·81 | 9·80 | — |

($\Delta pK = \log_{10} K_3/K_n$ where $K_n$ is the equilibrium constant for the reaction $(NPCl_2)_n + HCl \rightarrow (NPCl_2)_n,HCl$ in carbon tetrachloride.)

The trimeric chloride adds three moles of sulphur trioxide,[88] the addition compound, $(PNCl_2,SO_3)_3$, being obtained as a glassy mass which yields both sulphuric and sulphamic acids on hydrolysis, and decomposes thermally above 50°C. into chlorine, nitrogen, sulphur dioxide, thionyl chloride and sulphuryl chloride. The reaction of phosphonitrilic chloride trimer with sulphur trioxide and hydrogen chloride, or with chlorosulphonic acid, yields $PNS_2O_5Cl_4$, a colourless liquid, b.p. 55–6° at 0·02 mm., for which the formula $ClSO_2OPCl_2{=}NSO_2Cl$ has been suggested.[240] The adduct $(PNCl_2)_3,2AlCl_3$ has also been reported[27] as a pale yellow amorphous mass. There is little or no spectrophotometric evidence for the formation of complexes in solution between trimeric phosphonitrilic chloride and iodine,[223–4] benzene, hexamethylbenzene, *s*-trinitrobenzene, naphthalene, pyridine, methanol or chloranil,[224] though there is some cryoscopic evidence for a naphthalene complex.[225]

## PHOSPHONITRILIC POLYMERS

Some phosphonitrilic derivatives, principally the halides and isothiocyanates, form rubber-like high polymers on simple heating. Attention has been concentrated on the chlorides, particularly the trimer. Polymerization of the ordinarily-prepared material begins at about 250° and is rapid at 350°, though reaction is extremely slow at this temperature if the chloride is pure enough.[89] Depolymerization begins at higher temperatures, and the high polymer can be converted into a mixture of cyclic polymers by distillation *in vacuo*, provided that the temperature does not rise above 380°C.[90] The equilibrium among the lower polymers at 600° has been studied qualitatively,[90] and the polymerization shown to be exothermic.[90] The heats of polymerization of the cyclic chlorides have been measured directly by differential thermal analysis, and decrease steadily (per $PNCl_2$ group), the polymerization of the hexameric chloride being almost athermal.[91, 238]

| | $(PNCl_2)_3$ | $(PNCl_2)_4$ | $(PNCl_2)_5$ | $(PNCl_2)_6$ |
|---|---|---|---|---|
| Heat of Polymerization of $\frac{1}{n}(PNCl_2)_n$ ($-\Delta H$, kcal./mole) | 0·46 | 0·22 | 0·16 | 0·04 |

The kinetics of the polymerization of the trimeric and tetrameric chloride have been investigated, in bulk and in solution. An early claim[92] that oxygen was a catalyst was later withdrawn.[93] Later work[94–5] showed that the trimer polymerizes more rapidly than the tetramer[94] (its heat of polymerization is the greater[91]), that the rate is proportional to the concentration of the trimer,[95] and that the reaction is catalyzed by a number of oxygen-containing organic compounds (e.g. benzoic acid, acetone, ethanol, ethyl ether, methanol) and by some metals (zinc, tin, sodium). The specific rates per mole of catalyst are not very different,[94–5] suggesting that the reactions are all catalyzed by the same entity, and that the mechanism is the same in all cases. The authors propose an ionic mechanism,[95] the rate-determining step being the bimolecular reaction between a linear radical-ion $P_3N_3Cl_5^+$ and a neutral molecule $P_3N_3Cl_6$. Simple radical initiation seems unimportant; neither $\gamma$-radiation,[96] high energy electrons[212] nor ultra-violet radiation causes polymerization, though 50 kv. *X*-rays are more effective, especially just below the melting point.[213] The catalysis observed with *tert*.-butyl peroxide[94] persists to too high a temperature for it to be due to methyl radicals. The rate of polymerization of the trimeric chloride, as catalyzed by benzoic acid, has been investigated[97] over the range 200–220°, the rate constant conforming to the general equation $k(\text{min.}^{-1}) = 2{\cdot}75 \times 10^8 e^{-24{,}300/RT}$. The rate of depolymerization[98] of the high polymer is first-order in the high polymer, the rate constant being given by $k(\text{min.}^{-1}) = 4{\cdot}5 \times 10^7 e^{-26{,}000/RT}$. The activation energy is subject to an uncertainty of ±2 kcal./mole.

Like natural rubber, stretched polyphosphonitrilic chloride gives an *X*-ray fibre-diagram.[99] An approximate structure has been worked out, in which the $PNCl_2$ groups form a helical chain.[99–100] Measurements of elastic moduli[99, 101] show that polyphosphonitrilic chloride can be regarded as a linear polymer without cross-links, and they have also been used[102–3] to obtain approximate values of the molecular weight ($3{\cdot}7$–$7{\cdot}8 \times 10^4$). Higher, and probably more reliable, values have been obtained[104] by light-scattering measurements ($2{\cdot}18$–$3{\cdot}17 \times 10^5$) but the values depend, in any case, on the method of preparation of the sample.

The rate of hydrolysis of polymeric phosphonitrilic chloride in aqueous acetone is first-order in the polymer for part of its course, the rate constant at 25°C. being $5{\cdot}48 \pm 0{\cdot}28 \times 10^{-3}$ min.$^{-1}$, but the reaction does not go to completion.[105] Linear phosphonitrilic chlorides of general formula $(PNCl_2)_n$,HCl, where $n$ is about 14, are polymerized further by the action of a little water.[26] All the chlorine in them can be replaced by methoxy groups, about 10% of the methyl groups migrating in the sense

$$\text{—P(OMe)}_2\text{=N—} \rightarrow \text{P(O)(OMe)—NMe—}$$

The same chlorides react with sodium *tert.*-butoxide with the formation of sodium polymetaphosphimates and *iso*butylene.[26] Complete replacement of the chlorine in the high polymer by methoxy-groups has been achieved.[57] For the effect of high-energy electrons in promoting a combined esterification and polymerization see Ref. 83.

Polymerization of phosphonitrilic chloride trimer at pressures of 10 kbars and above indicates that increasing pressure favours the formation of the rubbery high polymer thermodynamically but is kinetically unfavourable. There appears to be no difference in the hydrolytic or thermal stability between the polymer formed at high pressures and that obtained at 1 atm.[171] Graft co-polymers between phosphonitrilic chloride polymer and styrene prepared by irradiation techniques show a reduced susceptibility to hydrolysis.[172]

Trimeric phosphonitrilic fluoride can also be polymerized by heat.[41] Polyphosphonitrilic fluoride remains rubber-like down to very low temperatures (−78°), but is even more susceptible to atmospheric moisture than the chloride.[42] Polymerization of the trimeric[49] and tetrameric[50] isothiocyanates occurs at a comparatively low temperature (150°).

Neither alkyl[36–7] nor aryl[38] derivatives polymerize further on heating; the former decomposes instead. Secondary reactions also occur on heating many other phosphonitrilic derivatives. The trimeric anilide loses aniline reversibly on heating,[68] insoluble phosphams of formula (NP:NPh) being eventually formed. Diethyl ether is eliminated irreversibly from hexa-ethoxy triphosphonitrile[56]; migration of alkyl groups from oxygen to nitrogen occurs at the same time,[26, 56] and saturated[37] and unsaturated hydrocarbons may be eliminated. It is probable that similar eliminations occur in the polymerization of phosphonitrilic derivatives of phenols and anilides.[106] Inorganic polymerization processes, including condensation reactions, have been reviewed.[107]

In many cases, the failure of thermal polymerization is more likely to be due to easy decomposition of the groups attached to phosphorus than to the intrinsic instability of the high-polymeric phosphonitrilic chain itself. Polymeric phosphonitriles have been prepared at much lower temperatures in another way, which is based in principle on an earlier preparation of phosphinimines.[108] The equation for the general reaction is:

$$R_2PX + MN_3 \rightarrow R_2PN_3 + MX \rightarrow R_2PN + N_2 + MX$$

the halide being heated with an alkali metal azide in an inert solvent above the decomposition temperature of the azido-phosphine. In published examples M is lithium[109] or sodium,[110] R is bromine,[110] phenyl[110] or trifluoromethyl,[111] and X either chlorine or bromine. The products appear to be of intermediate size, the polymeric mixture of phenyl chloro-phosphonitriles having an average molecular weight above 5000.[110] The mixture of bromides (m.p. 23–40°) was converted into the elastomer on heating *in vacuo* at 195–200°. Similar treatment of the mixture of diphenyl phosphonitrile polymers[110] gave a 33% yield of the tetramer $(Ph_2PN)_4$, m.p. 319·5–320°. The polymeric bis-trifluoromethylphosphonitrile,[109] $[(CF_3)_2PN]_n$, has m.p. 90–94°, is amorphous to *X*-rays, and is very resistant to heat and to acids. Treatment with alkali results in partial hydrolysis, half of the trifluoromethyl groups being liberated as fluoroform.[109] Allyl triphosphonitrilate has been polymerized to low molecular weight products of considerable thermal stability.[233]

## STRUCTURE OF PHOSPHONITRILIC DERIVATIVES

There are some disagreements about individual assignments for the trimeric bromide,[248, 268–9, 288] chloride[111–2, 206–7, 253, 268] and fluoride,[113, 206, 268] though their infra-red and Raman spectra are all consistent with $D_{3h}$ symmetry. Force constants have been calculated for the trimeric chloride and fluoride.[273] Some force constants of the trimeric chloride have been calculated,[114] but the data on which they are based are not well established. Infra-red spectra of several trimeric phosphonitrilic esters have been determined,[115] and the main features of the infra-red spectra of trimeric and tetrameric derivatives compared.[58]

The detailed structure of the trimeric chloride was determined first by electron diffraction.[116] Later crystal structure determination[117–8] showed that the equality of bond lengths is maintained in the crystal, but the molecules are slightly deformed, probably by lattice forces. Structural information is collected in Table XI.

*Table XI.—Structural Information on Trimeric Phosphonitrilic Derivatives* $(NPR_2)_3$

| R = | Br[173] | Cl[117–8] | F[174] |
|---|---|---|---|
| L(P–R) Å. | 2·18 | 1·99 | 1·52 |
| ∠RPR | 103° | 102° | 99·5° |
| L(P=N) Å. | 1·53 | 1·59 | 1·56 |
| ∠NPN | 117° | 119·5° | 119·5° |
| ∠PNP | 123° | 120·0° | 120·5° |

*Structural Information on Tetrameric Phosphonitrilic Derivatives* $(NPR_2)_4$

| R = | $NMe_2$[175] | Me[176] | Cl[124] | F[127] |
|---|---|---|---|---|
| L(P–R) Å. | 1·68 | 1·80 | 1·99 | 1·51 |
| L(P=N) Å. | 1·58 | 1·60 | 1·58 | 1·51 |
| ∠RPR | 104° | 104° | 103° | 100° |
| ∠NPN | 120° | 120° | 121° | 122·5° |
| ∠PNP | 133° | 132° | 132° | 147° |

*Structural Information on Pentameric and Hexameric Phosphonitrilic Derivatives* $(NPR_2)_5$ *and* $(NPR_2)_6$

| *n* =<br>R = | 5<br>Cl[221] | 6<br>$NMe_2$[227] |
|---|---|---|
| L(P–R) Å. | 1·94–1·98 | 1·67 |
| L(P=N) Å. | 1·49–1·55 | 1·57 |
| ∠RPR | 102° | 103° |
| ∠NPN | 118·4° | 120° |
| ∠PNP | 148° | 147° |

The nuclear quadrupole spectrum of the trimeric chloride at 14° has four absorption frequencies at 27·630, 27·704, 27·834, 27·903 Mc. sec.$^{-1}$, consistent with the crystal structure,[119–21] though the Cl–P–Cl angles are rather large, and may imply a degree of bond bending.[274] Preliminary results[122] on the crystal structure of the trimeric bromide show that its molecular structure is similar to that of the chloride.

The Raman and infra-red spectra of the tetrameric chloride do not allow a unique assignment of molecular symmetry; they are most nearly in accord with a planar skeleton of symmetry $D_{4h}$,[268] though $D_{2d}$, in which only the phosphorus atoms would be in a plane, is not excluded.[112, 288] In the crystal[123–5] the molecule has $S_4$ symmetry. The symmetry $D_{4h}$ has also been suggested[208] for the tetrameric bromide, $(PNBr_2)_4$, though here again $S_4$ symmetry is possible in the crystal.[161, 288] Structural details are given in Table XI. The nuclear quadrupole spectra[119–20] indicate four

*Table XII.—The Infra-red and Raman Spectra*(a) *of Trimeric Phosphonitrilic Chloride* $(PNCl_2)_3$[112]

| Raman(b) (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) |
|---|---|---|
| 100 (*vw*, *p*?) | | 1040 *vw* |
| 162 (4, *dp*) | | 1060 *vw* |
| 173 (3, *dp*) | | 1092 *m* |
| 210 (3, *dp*) | | 1121 *m* |
| | 315 *w* | 1200 *m* |
| 340 (1, *dp*) | 336 *s* | 1218 *vs* |
| 365 (10, *p*) | | 1310 |
| 523 (0·5) | 522 *vs* | 1368 |
| 575 (1, *dp*) | | 1660 |
| 610 (0·5) | 612 *s* | 1750 |
| 670 (4, *p*) | 672 *s* | 1880 |
| | 690 *vw* | 1975 |
| | 740 *w* | 2025 |
| 785 (2, *p*?) | 782 *m* | 2075 |
| | 885 *s* | 2095 |
| | 990 *m* | |

(a) Raman intensities are estimated numerically on a scale of ten; *p*=polarized, *dp*=depolarized. For infra-red intensities, *vw*=very weak, *ms*=moderately strong.
(b) See also Ref. 113.

*Table XIII.—The Infra-red and Raman Spectra*(a) *of Tetrameric Phosphonitrilic Chloride* $(PNCl_2)_4$[112]

| Raman (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) | Raman (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) |
|---|---|---|---|
| 137 (6, *dp*) | | 538 (5, *p*) | |
| 158 (3, *dp*) | | | 579 *w* |
| 169 (8, *dp*) | | 590 (5, *dp*) | 590 *w* |
| 178 (8, *dp*) | | 620 (0·5) | 615 *vs* |
| 192 (5, *dp*) | | 668 (0·5) | |
| 259 (4, *dp*) | | 725 (0·5) | 730 *ms* |
| 300 (0·5) | | | 790 *s* |
| | 339 *vw* | 895 (1·0, *dp*?) | 895 *s* |
| 350 (1·5, *p*) | 355 *vw* | | 1315 *vs* |
| | 370 *w* | | 1700 *vw* |
| | 393 *w* | | 1860 *vw* |
| 404 (10, *p*) | | | 2020 *vw* |
| 434 (4, *p*) | | | 2060 *vw* |
| 512 (0·5, *p*?) | 512 (shoulder) | | 2200 *vw* |
| | 520 *vs* | | |

(a) Raman intensities are estimated numerically on a scale of ten; *p*=polarized, *dp*=depolarized. For infra-red intensities, *vw*=very weak, *ms*=moderately strong.

non-equivalent chlorine atoms, and are therefore inconsistent with the crystal structure determination, but the lines are of variable relative intensity, and may indicate contamination of the sample with a polymorphic form.[13]

The main features of the vibrational spectra[45, 113, 206, 268] of the tetrameric fluoride are consistent with a symmetry $C_{2h}$, but the deviation from planarity is probably small. In the crystal the symmetry of the ring, though not of the fluorine atoms, is experimentally indistinguishable from $D_{4h}$, though this high symmetry is not required by the space group.[127–8] Structural data for this molecule and for octakis-(dimethylamido) tetraphosphonitrile[131] are given in Table XI. The skeletal symmetry in this last molecule is close to $D_{2d}$. Data on the tetrameric bromide are not sufficient to establish the symmetry $D_{4h}$, which would be expected.[268] Numerical values of vibrational frequencies of $(PNCl_2)_3$,[112] $(PNCl_2)_4$,[112] $(PNF_2)_3$,[113] $(PNF_2)_4$,[113] $(PNBr_2)_3$, $(PNBr_2)_4$ and $(PNBr_2)_5$[248] are given in Tables XII–XVI. For other values see references 253, 268.

*Table XIV.—The Infra-red and Raman Spectra*[(a)] *of Trimeric Phosphonitrilic Fluoride* $(PNF_2)_3$[113]

| Raman (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) | Raman (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) |
|---|---|---|---|---|
| 280 *m* | | | 816 *w* | 1462 *mw* |
| 309 *mw* | | | 860 *vs* | 1490 *w* |
| 336 *vw* | *m* | | 887 *s* | 1546 *w* |
| | 372 *ms* | | 905 *mw* | 1557 *w* |
| | 465 *s* | 952 *w* | 975 *s* | 1580 *w* |
| 470 *mw* | | | 1005 *ms* | 1638 *w* |
| | 516 *s* | | 1026 *m* | 1815 *w* |
| | 534 *mw* | | 1055 *mw* | 1868 *w* |
| 567 *m* | | | 1137 *w* | 1936 *w* |
| | 582 *w* | | 1205 *mw* | 2060 *m* |
| | 635 *w* | | 1240 *mw* | 2090 *w* |
| | 735 *vw* | | 1305 *vs* | 2180 *w* |
| 743 *s* | | | 1350 *ms* | 2230 *m* |
| | 775 *vw* | | 1378 *mw* | 2310 *w* |
| | 793 *vw* | | 1393 *w* | |
| | 807 *w* | | 1432 *w* | |

(a) Intensities are indicated by *vw*=very weak, *ms*=moderately strong.

*Table XV.—The Infra-red and Raman Spectra*[(a)] *of Tetrameric Phosphonitrilic Fluoride* $(PNF_2)_4$[113]

| Raman (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) | Raman (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) | Infra-red (cm.$^{-1}$) |
|---|---|---|---|---|
| 306 *w* | | | 860 *m* | 1588 *mw* |
| | 400 *vw* | | 886 *m* | 1660 *w* |
| | 418 *w* | | 913 *ms* | 1720 *w* |
| | 467 *m* | 940 *w* | 943 *m* | 1880 *w* |
| | 490 *s* | | 977 *s* | 1910 *w* |
| | 515 *mw* | 1015 *w* | | 2055 *mw* |
| 560 *w* | | | 1217 *mw* | 2086 *mw* |
| 614 *m* | 608 *mw* | | 1292 *m* | 2150 *w* |
| | 623 *w* | | 1300 *w* | 2290 *w* |
| | 725 *w* | | 1425 *vs* | 2400 *w* |
| | 769 *vs* | | 1445 *vs* | |
| | 840 *m* | | 1515 *ms* | |

(a) Intensities are indicated by *vw*=very weak, *ms*=moderately strong.

Less is known of the higher homologues. The cyclic nature of the chlorides $(PNCl_2)_{5-8}$ is suggested by their low dipole moments[130] and their infra-red spectra[130]; it is proved by their $^{31}P$ NMR spectra, which show that all the phosphorus nuclei in the same polymer have the same environment.[13] The same conclusion follows for the fluorides from the details of the infra-red spectra,[45] especially the structure of the $PF_2$ symmetrical stretching bands, and from the fact that they are prepared from the cyclic chlorides. The electrical conductivity of the chlorides, however, is compatible with an ionization mechanism in the sense:

$$(PNCl_2)_3 \rightleftharpoons [P_3N_3Cl_5]^+ + Cl^-$$

rather than with the electronic conductivity to be expected from a purely aromatic system.[247, 278]

*Table XVI.—The Infra-red Spectra[(a)] of the Phosphonitrilic Bromides*[248]

| $P_3N_3Br_6$ |  | $P_4N_4Br_8$ |  | $P_5N_5Br_{10}$ |  |
|---|---|---|---|---|---|
| Nujol mull | $CS_2$ soln. | Nujol mull | $CS_2$ soln. | Nujol mull | $CS_2$ soln. |
|  |  |  |  | 334 *w* |  |
| 318 *w* |  |  |  | 360 *vw* |  |
|  |  | 311 *w* |  | 388 *s* |  |
| 440 *vs* |  |  |  | 402 *vw* |  |
| 480 *mw* |  | 382 *vw* |  | 418 *w* |  |
| 523 *s* |  | 415 *m* |  | 449 *m* |  |
| 543 *sh* |  | 451 *s* |  | 468 *w* |  |
|  |  | 497 *s* |  | 488 *w* |  |
| 846 *w* | 848 *w–m* | 519 *s* |  | 513 *s* |  |
|  | 970 *vw* |  | 681 *m–w* | 699 *m* |  |
|  | 1020 *vw* | 760 *w* | 756 *m* | 728 *m* | 719 *m* |
|  | 1080 *vw* | 868 *m* | 869 *m* | 840 *m* | 848 *w* |
|  | 1108 *vw* |  |  |  |  |
|  | 1128 *w–m* | 1160 *vw, sh* |  | 1252 *s* | 1265 *s* |
| 1170 *vs* | 1173 *vs* | 1250 *s* | 1270 *vs* | 1311 *s* | 1330 *s* |
| 1225 *w, sh* |  | 1300 *vw, sh* |  |  |  |
| 1270 *w, sh* | 1262 *w* |  |  |  |  |
| 1920 *w* |  |  |  |  |  |
| 1964 *w* |  |  |  |  |  |
| 2020 *w* |  |  |  |  |  |

[(a)] Intensities are indicated by *vw* = very weak, *w–m* = weak to medium, *vs* = very strong, etc., and *sh* = shoulder.

The equality of the P–N bonds in all the structures so far determined, and their shortness compared with the single P–N bond length of 1·78 Å.[131] in the phosphoramidate ion $[NH_3PO_3]^-$, suggest at least limited delocalization rather than the alternate single and double bonds formally required by the normal valencies of phosphorus and nitrogen. The P–N bond energy term (72·3 kcal.)[16] deduced from the heats of formation of the trimeric and tetrameric chlorides (below) is higher than expected for a single bond, and a similar conclusion follows from the heats of formation of the other compounds quoted, and from the high value of the P–N stretching frequency (1218 cm.$^{-1}$) of the trimeric chloride.[112]

| Compound | $P_3N_3Cl_6$ | $P_3N_3(OC_6H_{11})_6$ | $P_3N_3Me_6$ | $P_4N_4Ph_8$ | $P_4N_4Cl_8$ |
|---|---|---|---|---|---|
| $-\Delta H_f^\circ$ (c) | 194·1 | 582·0 | 125·1 | −40·7 | 259·2 |
| Ref. | 16 | 132 | 132 | 132 | 16 |

Since all the 3*p* orbitals of phosphorus are used in formation of four tetrahedrally-directed σ-bonds, the ring π-bonds must be formed by overlap of a 2*p*π-orbital on nitrogen and a 3*d*π-orbital on phosphorus. Two *d*-orbitals have the right symmetry to interact in this way. One is in a plane tangential to the ring, and perpendicular to it, the other is in a plane which bisects the NPN angle internally. The former is polarized more strongly by the ring nitrogen atoms, and has been supposed, on these grounds, to be the more strongly involved.[133–4] Delocalization energy is expected to increase steadily with ring size, in contrast to carbocyclic aromatics. If both $d\pi$-orbitals contribute equally,[135] delocalization occurs only in successive 3-centre PNP groups, and $\pi$-electron energies (per electron) should remain constant. The relative extents to which the two orbitals participate are not yet certain, but the reality of the $\pi$-bonding to which they both contribute is shown by the tendency of tetrameric molecules to approximate to $D_{2d}$ symmetry, a configuration which uniquely equalizes $\pi$-contributions round the ring, if the natural angles are too small for planarity.

The large angles at nitrogen, however, show that the lone pairs there are delocalized to some extent, the phosphorus atom acting as an acceptor, and so forming a second $p\pi$-$d\pi$ bond perpendicular to the first in the NPN plane. Two more $d$-orbitals are (unequally) involved in the formation of these new ($\pi'$) bonds, which are expected to reduce the base strength, and increase the torsional flexibility about the P–N bond. Molecular deformation appears particularly easy in the phosphonitrilic fluorides,[45] where the $\pi$- and $\pi'$-contributions would be most nearly equal, because of the high electronegativity of the fluorine atoms. The ultra-violet spectra are not decisive on the question of $\pi$-bonding. The chlorides absorb increasingly down to 2000 A.[13] or 1850 A. (trimer)[136] without reaching a maximum; the trimeric and tetrameric fluorides have intense peaks at 1494 ± 5 A. and 1475 ± 5 A., respectively.[136] The interpretation of the spectra is not yet known in detail, but the spectra of the chlorides are only slightly changed on solution of the compounds in sulphuric acid,[13] suggesting that the absorption is due to an $n \rightarrow \pi^*$ transition on the halogen atoms. Bonding problems in these compounds have been discussed,[177, 161] and further data on solvent effects on their ultra-violet and infra-red spectra have been presented.[226] $^{31}$P nuclear magnetic resonance chemical shifts have been recorded for a wide range of phosphonitrilic compounds.[270]

## APPLICATIONS OF PHOSPHONITRILIC DERIVATIVES

There are several proposed applications in the preparation of resins resistant to high temperatures. Phosphonitrilic derivatives improve the high-temperature properties of phenolic resins,[137] and can be used in the manufacture of semi-ceramic materials.[138] Polymeric phosphonitrilic chlorides have been used in conjunction with asbestos, glass, or other inorganic fibres to make insulating materials which are both flexible at ordinary temperatures and resistant to high temperatures.[139–41, 178] Trifluorophenoxy derivatives of phosphonitriles are fluids of high thermal stability.[271]

Resins are formed by condensation of the phosphonitrilic chlorides with butylamine[142]; the condensation products of phosphonitrilic chlorides with secondary and tertiary aromatic amides have been found to be compatible with other polymers.[143] The products of the reactions of phosphonitrilic chlorides with alcohols, phenols, naphthols, mercaptans or thiophenols have been suggested as plasticizers for resins, lacquers or varnishes.[144] Thermally stable low polymers are formed by the reaction of hexaphenyldichlorotetraphosphonitrile and diols.[254] Phosphonitrilic esters, prepared by the action of alcohol and pyridine on the rubber-like high polymer, can be used as plasticizers for nitrocellulose lacquers and films.[145] The phosphonitrilic chlorides have shown some advantage over other catalysts in the polymerization of low-molecular siloxanes,[146] and tertiary olefines can be polymerized[147] in contact with the monomeric phosphonitrilic chloride derivative, $PNCl_2,POCl_3$. The partial hydrolysis products of polyphosphonitrilic chlorides have been proposed[148] as constituents of heat-resisting paints.

Phosphonitrilic chlorides can be used in processes for the flame-proofing of fabrics.[179] The chlorine atoms can be substituted by hydroxy-, amino-, hydrazino- or other groups, resinous materials being formed with or without the use of cross-linking agents.[149] Amino-derivatives of the phosphonitrilic chlorides can also be used directly.[12] The use of the condensation product of a phosphonitrilic polymer with a chloro-aniline and a polyamino compound ensures that flame-proofing properties are retained after repeated laundering.[150] Useful flame-proofing properties are also obtained from the reaction product of phosphonitrilic polymers and a 2:3 dihaloalcohol,[151] and, particularly, from the addition products of unsaturated phosphonitrilic esters and saturated polyhalogeno-hydrocarbons.[152]

The phosphonitrilic chlorides[153] and their derivatives[144, 154] have also been suggested as oil additives, with the object of obtaining increased load capacity, viscosity index and resistance to corrosion. Pour-point depressants have been prepared by polymerizing phosphonitrilic esters in the presence of a Friedel–Crafts catalyst.[155] Phosphonitrilic compounds may also be of use as hydraulic fluids[144] and as fuel additives in internal combustion engines, where they decrease cylinder deposits.[156] The products obtained by reaction of a phosphonitrilic chloride polymer with a fluoroarylhydroxy or fluoroalkarylhydroxy compound are used as hydraulic fluids, transformer oils and heat exchange fluids.[180, 260] Phosphonitrilic chlorides have also been tested for their effectiveness in the control of surface ignition.[157]

A heat resistant plastic dielectric has been obtained from a resin containing phosphonitrilic chloride, diphenylsilanediol and asbestos,[181] and polymeric phosphonitrilic chlorides have been used as binders for abrasive wheels.[182] Products with semiconductor properties are reported to be formed by copolymerization of phosphonitrilic chloride and acrylonitrile.[183] Phosphonitrilic chloride trimer or tetramer can be used as a photographic hardening agent.[184] Aziridinyl phosphonitrile derivatives are powerful insect sterilants.[285]

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### SECTION XIX

# PHOSPHORUS PSEUDOHALIDES

### BY A. F. CHILDS

CYANIDES, cyanates and thiocyanates are frequently referred to as pseudo-halides or halogenoids, since they can show a close chemical and physical resemblance to halides. The pseudohalide derivatives of phosphorus are no exception to this rule. For example, the hydrolysis of phosphorus(III) halides and pseudohalides follows the same general course:

$$PX_3 + 3H_2O \rightarrow HPO(OH)_2 + 3HX \qquad (X = F, Cl, Br, I, CN, OCN, SCN)$$

Furthermore such phosphorus pseudohalides can be prepared by metathesis between phosphorus halides and metal pseudohalides, while intermediate mixed halide–pseudohalides, such as $POCl_2(OCN)$, can be isolated in many cases. For these reasons it was thought desirable to discuss the phosphorus pseudohalides in the present work, although they had not been treated in the previous edition. Derivatives of other pseudohalides (–SeCN, –TeCN, $-N_3$, –OCl) have not apparently received any attention.

The phosphorus(III), phosphoryl and thiophosphoryl cyanides, cyanates and thiocyanates are covalent compounds. In their behaviour they broadly resemble the corresponding bromides or iodides, though exhibiting certain additional reactions typical of the pseudohalogen radical. A study of their behaviour[1] suggests that the stability of the P–X bond is in the order:

$$F > Cl > Br > CN > I > SCN \qquad (\simeq OCN\ ?).$$

Many of the pseudohalides polymerize at room temperature, or more rapidly when heated, to give solids of unknown composition.

Cyanides, cyanates and thiocyanates can each exist in one of two isomeric forms, and the structure of the phosphorus compounds has been a matter of some debate. Phosphorus(III) cyanide has been firmly established as a cyanide, $P(-C{\equiv}N)_3$ by an *X*-ray crystal structure determination,[2] while the infra-red spectrum of diphosphorus tetracyanide[3] and the mass spectrum of phosphorus(III) cyanide difluoride[4] suggest that these have a similar structure. However, molar refractivity[5] and infra-red[6] studies show that $P(NCS)_3$ and $PO(NCS)_3$ are both *iso*thiocyanates, while $P(NCO)_3$, $PO(NCO)_3$[7] and $P_2(NCO)_4$[8] all appear to have an *iso*cyanate structure. Much more evidence is required before any general rule can be established.

The stability of compounds containing both halide and pseudohalide groups is very variable. Some compounds, such as $PF(NCO)_2$, $PF_2(NCS)$, $PCl_2(NCO)$, $POCl_2(NCO)$, are relatively stable and can be stored for long periods at room temperature without disproportionation. Others (e.g., $PCl(NCO)_2$,[9] $PCl(NCS)_2$, $PCl_2(NCS)$[10]) slowly disproportionate even at room temperature, while others again ($PF_2(NCO)_2$,[9] $PBr_2CN$,[11] $PF_2CN$ [4]) are so unstable that they can hardly be prepared in the pure state. As yet there seems to be no general theory which correlates this behaviour.

## PHOSPHORUS CYANIDES AND *ISO*CYANIDES

### Phosphorus(III) Cyanide

Although crude specimens of phosphorus(III) cyanide may have been obtained earlier by the interaction of phosphorus and mercuric cyanide,[12–13] this substance was first obtained reasonably pure by the reaction of phosphorus(III) chloride with silver cyanide,[14–15] a method still recommended for its preparation. In a typical procedure,[16] dry silver cyanide and phosphorus(III) chloride were heated together in an evacuated sealed tube at 105°–150°C. for 24–8 hr. After excess phosphorus(III) chloride had been distilled off, the residue was sublimed under a high vacuum at 120°C. Variations of this preparation have been reported.[1,17] Other workers have carried out the reaction in an anhydrous solvent under reflux,[18] and by passing phosphorus(III) chloride vapour over silver cyanide in a heated tube.[19] Phosphorus(III) cyanide has also been obtained by the reaction of silver cyanide with phosphorus(III) bromide[11,21] or phosphorus(V) chloride,[1,15] or by the interaction of phosphorus(III) chloride with trimethylcyanosilane.[22]

Phosphorus(III) cyanide forms white needles or plates, m.p. 200–203°C., which sublime only a few degrees above the melting point.[15] It is only slightly soluble in chloroform, ether, carbon disulphide, phosphorus(III) chloride,[15] carbon tetrachloride or benzene,[18] but dissolves to about 15% in acetonitrile.[16]

The crystals of phosphorus(III) cyanide are tetragonal, of space group $I\bar{4}2d$, having 16 molecules in a unit cell, dimensions $a = b = 14{\cdot}00$, $c = 10{\cdot}81$ Å. From their acicular habit, it is possible that the crystals may be monoclinic at the sublimation temperature and transform to the tetragonal form on cooling.[2] The same study showed that the compound has the cyanide structure, $P(C{\equiv}N)_3$. The molecule is pyramidal with $C_{3v}$ symmetry, having $P{-}C = 1{\cdot}78$, $C{\equiv}N = 1{\cdot}15$ Å., $<C{-}P{-}C = 93°$ and $<P{-}C{\equiv}N = 172°$.[2] The non-linearity of the $P{-}C{\equiv}N$ group is unexpected, and is perhaps due to interactions in the crystal which may not occur in the isolated molecule.[23]

Two studies of the infra-red and Raman spectra of phosphorus(III) cyanide were in general agreement,[16,23] though the conclusions differed from those of earlier workers.[17] The fundamental frequencies suggested ($a_1$; 2206, 620, 468, 145: $e$; 2202, 581, 452, 314, 159 cm.$^{-1}$) accord with the $C_{3v}$ symmetry deduced from the crystallographic study.[23] Force constants have been calculated from these data.[24] The $^{31}P$ nuclear magnetic resonance spectrum shows a chemical shift $\delta_P$ of $+135{\cdot}7$ p.p.m.[21]

Phosphorus(III) cyanide is very reactive substance, and should be handled in a dry inert atmosphere.[16] Under these conditions it appears to be indefinitely stable at room temperature, and melts without decomposition, but prolonged heating leads to polymerization, with formation of a reddish brown solid.[18] In air it ignites when touched with a warm rod,[15,18] and it is rapidly decomposed by atmospheric moisture with the formation of hydrogen cyanide, phosphorous acid and a yellow amorphous material of high phosphorus content[1,15,18] which may be a sub-cyanide.[16]

The reaction with water is violent, the main products being phosphorous acid and hydrogen cyanide:

$$3H_2O + P(CN)_3 \rightarrow HPO(OH)_2 + 3HCN$$

However, particularly in neutral solution, a small amount of phosphine is formed,[19] perhaps by local overheating of intermediate hydrolysis products, since it is not observed when ice cooling is employed.[1] In alkaline solution phosphite is still the main product, but several other phosphorus oxyanions are formed, as shown earlier (page 472).[25] The analogous reaction with tritium oxide has been used to prepare tritium cyanide.[26] Alcohols react similarly to give trialkyl phosphites and hydrogen cyanide:

$$3ROH + P(CN)_3 \rightarrow P(OR)_3 + 3HCN$$

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although alkyl cyanide is also obtained[15] presumably by some such reaction as:

$$3ROH + P(CN)_3 \rightarrow HPO(OR)_2 + RCN + 2HCN$$

There is no reaction with dry ammonia in the cold, but when heated a black insoluble material of unknown composition is formed.[15]

### Mixed Phosphorus(III) Cyanide Halides

An attempted preparation of phosphorus(III) bromide dicyanide by reaction of the appropriate quantities of phosphorus(III) bromide and silver cyanide yielded only phosphorus(III) cyanide and unchanged bromide.[11] Hence either the bromocyanide was formed and then disproportionated, or the intermediate bromocyanides are considerably more reactive towards silver cyanide than is phosphorus(III) bromide itself. Phosphorus(III) cyanide difluoride has, however, been prepared by the reaction of phosphorus(III) difluoride iodide with copper(I) cyanide. It is a colourless volatile liquid which disproportionates appreciably to $PF_3$ and $P(CN)_3$ in 1 hr. at $-20°$. The $^{19}F$ and $^{31}P$ nuclear magnetic resonance spectra support the formula $F_2PCN$, while the infra-red and Raman spectra are compatible with a pyramidal ($C_s$) structure.[4]

### Diphosphorus Tetracyanide (Phosphorus Dicyanide) $P_2(CN)_4$

Diphosphorus tetraiodide reacts with silver cyanide in an inert solvent, yielding $P_2I_n(CN)_{4-n}$ ($n < 4$). The reaction is favoured by use of an excess of silver cyanide, and polar solvents such as $CH_3CHCl_2$. Diphosphorus tetracyanide is isolated by precipitation with petroleum ether or by fractional crystallization. It is a white solid, very sensitive to oxidation and hydrolysis, which disproportionates and polymerizes without melting or subliming. The infra-red spectrum, with bands at 2199, 2275 and 628 cm.$^{-1}$, suggests a cyanide ($P–C{\equiv}N$) structure analogous to that of phosphorus(III) cyanide.[8] In view of the instability of diphosphorus tetracyanide, the failure of a previous attempt to obtain it by reduction of phosphorus(III) cyanide with phosphorus at 210°[15] is not surprising.

### Phosphorus(V) Cyanide

The reaction of phosphorus(V) chloride with silver cyanide at room temperature yields only phosphorus(III) cyanide, together with cyanogen[1] or cyanogen chloride.[15] However, at $-39{\cdot}5$°C. the pressure over a mixture of phosphorus(III) cyanide and cyanogen falls to a constant value of 12·4 mm. This presumably represents the dissociation pressure of phosphorus(V) cyanide, since it lies between the initial vapour pressure of the cyanogen and that of pure phosphorus(III) cyanide.[1]

## PHOSPHORUS CYANATES AND *ISO*CYANATES

### Phosphorus(III) *Iso*cyanate

Phosphorus(III) *iso*cyanate was first prepared by reaction of phosphorus(III) chloride with silver cyanate in benzene,[27] a procedure which is still much used. Other workers have used lithium cyanate[28]; sodium or potassium cyanate in a polar solvent such as acetonitrile, nitromethane, acetone,[29] or liquid sulphur dioxide[30]; or cyanic acid in the presence of an acid acceptor.[31] The reaction of phosphorus(III) iodide with silver cyanate in nitromethane also yields the *iso*cyanate,[32] as does the disproportionation of the mixed phosphorus(III) chloride *iso*cyanates.[33]

Phosphorus(III) *iso*cyanate is a colourless liquid; b.p. 169·3°/760 mm.,[27] 78°/20 mm.,[30] 64–6°/10 mm.[29]; m.p. −2°,[27,34] refractive index for white light 1·5352,[27] 1·5329/25°.[31] Other properties of the pure liquid are recorded in Table I. On standing the substance slowly solidifies, forming a white solid, m.p. 80–95°, which can be reconverted to the original *iso*cyanate, b.p. 169°, by distillation.[7,27,34] The molecular weight of this new solid is unknown, but its formation is accompanied by the appearance of a second peak in the gas–liquid chromatogram,[7] and polymerization is presumably involved.

The infra-red and Raman spectra support an *iso*cyanate structure (P–N=C=O) for the molecule[7,34] and can best be explained by assuming $C_{3v}$ symmetry,[7,35–36] although it is not established whether the P–N=C=O groups are linear or bent.[7] The liquid is transparent in the ultra-violet region above 2300 A.[7,37] The nuclear magnetic resonance spectrum has been recorded.[38]

A study of the use of phosphorus(III) *iso*cyanate as a solvent (specific conductivity $1{\cdot}89 \times 10^{-5}$ ohm$^{-1}$/25°) showed that while it dissolved many organic compounds, inorganic compounds and elements tested were insoluble. Sulphuric acid, silver nitrate, acetic acid and acetaldehyde reacted violently.[34]

Phosphorus(III) *iso*cyanate also reacts rapidly with water,[32,34] and must be handled in a dry atmosphere. The products of hydrolysis by alkali have been discussed[25] (see page 472). Although, unlike phosphorus(III) cyanide, the *iso*cyanate does not inflame on warming in air, it is rapidly oxidized by nitrogen dioxide[39] or sulphur trioxide[30] forming phosphoryl cyanate. Iodine dissolves slowly in phosphorus(III) *iso*cyanate giving a red-brown solution (cf. the violet solution in $PCl_3$) from which an orange solid with the formula $P(NCO)_3I$ can be isolated. This may be analogous to $PCl_3I$ (Mellor, VIII, 1045). Chlorine, on the other hand, reacts vigorously to give a yellow oil, which forms a yellow solid on treatment with carbon tetrachloride. This solid may be a phosphorane, $P(NCO)_3Cl_2$, since it yields phosphate on hydrolysis,[40] although the evidence does not exclude the possibility of its being $PCl_5$.

Phosphorus(III) *iso*cyanate undergoes exchange reactions with other covalent compounds, the course of which is governed by the distillation of the most volatile component. Thus benzoyl chloride and mercuric chloride yield phosphorus(III) dichloride *iso*cyanate, or chloride di-*iso*cyanate, while aluminium chloride forms phosphorus(III) chloride and aluminium cyanate.[41] Alkyl or aryl *iso*cyanatidites are formed by reaction with the corresponding phosphites.[42]

The incorporation of phosphorus(III) *iso*cyanate in phenol-formaldehyde,[43] polyurethane,[44] epoxy[45] or polyester[46] resins has been claimed to improve their resistance to combustion, and their adhesion to wood or metal, while resins have been obtained by its reaction with aldehydes (e.g., PhCHO), hydroxyl or amino-compounds.[20,47] The *iso*cyanate has less effect on the octane rating of gasoline than phosphorus(III) *iso*thiocyanate.[48]

## MIXED PHOSPHORUS(III) *ISO*CYANATE HALIDES

### Phosphorus Fluoride *Iso*cyanates

If phosphorus(III) *iso*cyanate is heated with powdered sublimed antimony(III) fluoride a mixture of phosphorus(III) fluoride di-*iso*cyanate, $PF(NCO)_2$, and difluoride *iso*cyanate, $PF_2(NCO)$, is formed, and may be separated by fractional distillation.

Phosphorus fluoride di-*iso*cyanate is a colourless liquid, b.p. 98·7°C., f.p. −55·0°C., refractive index (20°, white light) 1·4678, molecular refractivity 25·25. Other properties are listed in Table I. The liquid shows a critical solution temperature of −16° in carbon disulphide.

*Table I.—Physical Properties of the Phosphorus* Isocyanates

| Compound | Boiling point °C.(a) | Freezing point °C. | Density (g./c.c.) | Constants in vapour pressure equation $\log p_{(\mathrm{mm.})} = A - B/T$ |  | Latent heat of vaporization kcal./mole | Trouton's constant g.-cal./deg.K. | Ref. |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | $A$ | $B$ |  |  |  |
| $P(NCO)_3$ | 169·3 | −2 | 1·439 | 8·7455 | 2595 | 11·9 | 26·8 | 27 |
|  | 64–6/10 mm. |  |  |  |  |  |  | 29 |
|  | 78/20 mm. |  |  |  |  |  |  | 30 |
| $P(NCO)_2F$ | 98·7 | −55·0 | 1·475/20° | 8·3210 | 2022·7 | 9·25 | 24·8 | 9 |
| $P(NCO)F_2$ | 12·3 | ~ −108 | ~ 1·444/20° | — | — | — | — | 9 |
| $P(NCO)_2Cl$ | 134·6 | −50 | 1·505/20° | 8·87981 | 2045·2 | 11·2 | 27·4 | 33 |
|  | 67–8/50 mm. |  |  |  |  |  |  |  |
| $P(NCO)Cl_2$ | 104·5 | −99 | 1·513/20° | — | — | — | — | 49 |
| $PO(NCO)_3$ | 193·1 | +5 | 1·570 | 9·1682 | 2931 | 13·41 | 28·8 | 50 |
|  | 88/10 mm. |  |  |  |  |  |  | 30 |
| $PO(NCO)F_2$ | 68–68·5 | — | 1·5899/24° | 7·15 | 1880 | 8·6 | 25·2 | 51 |
|  | 69 |  |  |  |  |  |  | 52 |
|  | 68 |  |  |  |  |  |  | 53 |
| $PO(NCO)Cl_2$ | 136–8 (decomp.) | — | 1·649/15° | ~ 8·79(b) | ~ 2390(b) | ~ 10·9(b) | ~ 26·6(b) | 54 |
|  | 72–5/100 mm. |  |  |  |  |  |  | 55 |
|  | 60–4/50 mm. |  |  |  |  |  |  | 51 |
|  | 55–8/20 mm. |  |  |  |  |  |  | 56 |
|  | 45–6/20 mm. |  |  |  |  |  |  | 57 |
|  | 36–7/8 mm. |  |  |  |  |  |  | 58 |
|  | 19·7–20/5 mm. |  |  |  |  |  |  | 54 |
| $PO(NCO)FCl$ | 101–3 | — | — | — | — | — | — | — |
| $PS(NCO)_3$ | 215 (decomp.) | 8·8 | 1·538 | 10·032 | 3492 | 16·0 | 33 | 59 |
|  | 135/30 mm. |  |  |  |  |  |  |  |

(a) At 760 mm. Hg unless stated otherwise.
(b) Rough estimate from recorded boiling points.

Phosphorus difluoride *iso*cyanate has a much lower stability (cf. $PF_2Br$) and rapidly gives phosphorus(III) fluoride on distillation, even at −35°, though it may be stored for a few days in a closed vessel at 0°. Like $PF(NCO)_2$ it is a colourless liquid with an unpleasant irritating odour, b.p. 12·3°C., f.p. ~ −108°C., refractive index (4·4°, white light) ~ 1·3695, molecular refractivity ~ 17·38. Both compounds are hydrolyzed by water, $PF(NCO)_2$ about as fast as $PCl_3$, $PF_2(NCO)$ somewhat less readily. $PF(NCO)_2$ does not add sulphur at temperatures up to 143°C.[9]

## Phosphorus Chloride *Iso*cyanates

Gradual addition of silver cyanate to excess of phosphorus(III) chloride, either alone or in the presence of a solvent such as carbon disulphide or benzene, similarly gives a mixture of phosphorus(III) chloride di-*iso*cyanate and dichloride *iso*cyanate, which can be separated by distillation.[49] The interaction of phosphorus(III) *iso*cyanate with phosphorus(III) chloride,[10, 49] benzoyl chloride, or mercuric chloride,[41] also gives small yields of these mixed chloride *iso*cyanates. Ligand exchange between phosphorus chloride and *iso*cyanate is slow at room temperature but accelerated by heating,[38] though accurate equilibrium data could not be obtained because of the instability of $P(NCO)_3$.[10]

Phosphorus(III) chloride di-*iso*cyanate, $PCl(NCO)_2$, is a colourless liquid, b.p. 67–8°/50 mm., 134·6°/760 mm. (extrap.), m.p. −50°C.[33] It fairly rapidly disproportionates on standing, yielding phosphorus(III) *iso*cyanate and phosphorus(III) dichloride *iso*cyanate, $PCl_2(NCO)$. This decomposes more slowly (6% in 4 months at room temperature). It is a colourless liquid, b.p. 104·5°, m.p. −99°.[49] Other properties of these compounds are given in Table I.

## Phosphorus Bromide *Iso*cyanates

Ligand exchange between phosphorus(III) bromide and phosphorus(III) *iso*cyanate is fairly rapid at 80°, but mixed *iso*cyanates have not been isolated, although their $^{31}P$ nuclear magnetic resonance spectra have been recorded.[38]

## Phosphoryl *Iso*cyanate

Phosphoryl *iso*cyanate, $OP(NCO)_3$, can be prepared by the action of silver cyanate on phosphorus(III) cyanate in refluxing benzene. Only a low yield of the desired product is obtained, together with a large amount of a water-sensitive, yellowish solid of high melting point, which is formed by polymerization. Better yields are reported from the oxidation of phosphorus(III) *iso*cyanate with $NO_2$ in carbon tetrachloride[39] or sulphur trioxide in liquid sulphur dioxide.[30]

Phosphoryl *iso*cyanate is a colourless liquid, b.p. 193·1°/760 mm. (extrap.)[50] 88°/10 mm.,[30] m.p. 5°, refractive index 1·4804.[50] When heated it is slowly converted to the insoluble polymer mentioned above. The infra-red and Raman spectra of phosphoryl *iso*cyanate closely resemble those of phosphorus(III) *iso*cyanate, with the addition of two phosphoryl vibrations,[7] and like that compound it probably has trigonal pyramidal ($C_{3v}$) symmetry.[7, 35, 36] The ultra-violet spectrum shows a weak absorption at 2660 Å.[7, 37]

Phosphoryl *iso*cyanate has been claimed to give the properties of flame resistance, and adhesion to metal or other surfaces, to cellulose,[60] phenol-formaldehyde,[43] polyurethane,[44] epoxy[45] and other resins.[61] It has also been used to coat pigments for use in polyurethanes[62] and to form polymers with inorganic materials containing active hydrogen.[47]

**Refs. p. 594**

## MIXED PHOSPHORYL *ISO*CYANATE HALIDES

### Phosphoryl Fluoride *Iso*cyanates

Phosphoryl difluoride *iso*cyanate, POF$_2$(NCO), was first prepared by the reaction of antimony(III) fluoride with phosphoryl dichloride *iso*cyanate.[51] It has also been obtained by the interaction of phosphorodifluoridic anhydride with potassium cyanate[52]:

$$F_2P(O)OP(O)F_2 + KOCN \rightarrow F_2P(O)NCO + KPO_2F_2$$

or of silicon tetra*iso*cyanate with phosphoryl fluoride[53]:

$$Si(NCO)_4 + 4POF_3 \rightarrow 4F_2P(O)NCO + SiF_4$$

It is a colourless liquid, b.p. 68–68·5/760 mm.,[51] $n_{\mathrm{D}}^{25}$ 1·3381, $d_4^{24}$ 1·5899. Other physical properties are given in Table I, and the $^{19}$F and $^{31}$P nuclear magnetic resonance spectra in Table II. The infra-red spectrum has been reported.[52, 53]

Phosphoryl difluoride *iso*cyanate is stable at room temperature in a dry atmosphere,[51] but polymerizes to a yellow solid if heated.[53] It is rapidly hydrolyzed by water, and reacts with alcohols or phenols to give difluorophosphoryl carbamates, F$_2$PONHCOR, and with amines, giving the analogous ureas, F$_2$PONHCONHR.[51] It has been claimed to inhibit the growth of plants[63] and to stabilize liquid ozone.[64]

Phosphoryl chloride fluoride *iso*cyanate, POClF(NCO), is a by-product from the reaction of antimony fluoride with phosphoryl dichloride *iso*cyanate. It is a liquid, b.p. 101–103°C., $n_{\mathrm{D}}^{25}$ 1·4024.[51]

*Table II.—Nuclear Magnetic Resonance Data on the Phosphorus* Iso*cyanates and Related Compounds*

| Compound | $^{31}$P N.M.R. spectrum | | Line intensity | Ref. |
|---|---|---|---|---|
| | Coupling constant $J_{P\text{–}F}$, c.p.s. | Chemical shift $\delta_P$ p.p.m.[(b)] | | |
| P(NCO)$_3$ | — | −97·0 | — | 38 |
| P(NCO)$_2$F | 1226 | −127·9 | — | 38 |
| P(NCO)F$_2$ | 1310 | −130·6 | — | 38 |
| PF$_3$ | 1420 | −97·0 | — | 38 |
| P(NCO)$_2$Cl | — | −128·0 | — | 38 |
| P(NCO)Cl$_2$ | — | −165·7 | — | 38 |
| PCl$_3$ | — | −220·0 | — | 38 |
| P(NCO)$_2$Br | — | −126·0 | — | 38 |
| P(NCO)Br$_2$ | — | −167·0 | — | 38 |
| PBr$_3$ | — | −229·0 | — | 38 |
| PO(NCO)$_3$ | — | +40·9 | — | 38 |
| PO(NCO)F$_2$[(a)] | 1000 | 29·5 | 1:2:1 | 52 |
| | 1007 | 30 | 1:2:1 | 53 |
| PO(NCO)$_2$Cl | — | 26·6 | — | 38 |
| PO(NCO)Cl$_2$ | — | 9·2 | — | 38 |
| POCl$_3$ | — | −2·2 | — | 38 |

(a) PO(NCO)F$_2$ has a $^{19}$F N.M.R. spectrum with $J_{F\text{–}P}$ = 998 c.p.s., $\delta_F$ +72·2,[52] 72·0[53] p.p.m. with respect to CCl$_3$F.

(b) Reference standard 85% H$_3$PO$_4$.

### Phosphoryl Chloride *Iso*cyanates

Phosphoryl dichloride *iso*cyanate, $POCl_2(NCO)$, is commonly made by the reaction of phosphorus(V) chloride with methyl or ethyl carbamate.[54,57] The reaction appears to proceed through the intermediate formation of a N-carboalkoxyiminophosphoryl chloride, which is stable at 0–10°, but decomposes at 20–40°, with evolution of alkyl chloride[57,65]:

$$PCl_5 + H_2NCOOR \xrightarrow{0-10^\circ}$$

$$Cl_3P = N{\cdot}COOR(+2HCl) \xrightarrow{20-40^\circ} Cl_2PO(NCO)(+RCl)$$

If carried out cautiously the reaction gives an excellent yield of product, but the second stage can be very violent or even explosive, and is often moderated by carrying it out in a solvent, such as methylene chloride[56] or ethylene chloride.[66,67] Alternatively, an N-substituted carbamate can be used:

$$Me_2NSO_2NHCOOR + PCl_5 \xrightarrow{85-115^\circ} Cl_2PO(NCO) + Me_2NSO_2Cl + HCl + RCl$$

but this involves the fractional distillation of the dichloride *iso*cyanate from dimethylaminosulphonyl chloride.[55] Ligand exchange in the system $POCl_3$–$P(NCO)_3$ has been shown to be a slow process, even on prolonged heating.[38]

Pure phosphoryl dichloride *iso*cyanate is a colourless liquid, b.p. 19·7–20·0°/5 mm.,[54] 45–6°/20 mm.,[57] 136–8° (decomp.)/760 mm.,[54] $n^{21} = 1{\cdot}4682$,[58] $n_D^{15} = 1{\cdot}470$,[54] $d_4^{15} = 1{\cdot}649$ g./c.c.[54] The infra-red spectrum has been reported.[81] It reacts with small quantities of water giving N-dichlorophosphoryl carbamic acid[68,69]:

$$Cl_2PONCO + H_2O \rightarrow Cl_2PONHCOOH$$

The reaction is best carried out by the addition of the *iso*cyanate to 36% aqueous hydrochloric acid in carbon tetrachloride at −20°, followed by gentle warming of the mixture to 20°, when the carbamic acid crystallizes out. N-Dichlorophosphoryl carbamic acid decomposes above 73°, giving some phosphoryl dichloride *iso*cyanate, together with a residue of $HOPO({=}NCOOH)_x$, which decomposes further to $(N{=}PO(OH))_x$ and $(PON)_x$ at higher temperatures. Phosphorus(V) chloride converts the carbamic acid to phosphoryl dichloride *iso*cyanate:

$$Cl_2PONHCOOH + PCl_5 \rightarrow Cl_2PO(NCO) + POCl_3 + 2HCl^{69}$$

Phosphoryl dichloride *iso*cyanate reacts analogously with alcohols or phenols to give N-dichlorophosphoryl carbamates:

$$Cl_2PO(NCO) + ROH \rightarrow Cl_2P(O)NHCOOR$$

and with amines to give ureas:

$$Cl_2PO(NCO) + RR'NH \rightarrow Cl_2P(O)NHCONRR' \rightarrow (RR'N)_2P(O)NHCONRR'^{54}$$

### Thiophosphoryl *Iso*cyanates

Thiophosphoryl *iso*cyanate, $PS(NCO)_3$, has been obtained in poor yield together with much polymeric material by the addition of sulphur to phosphorus(III) *iso*cyanate in a sealed tube at 140°. The direct reaction of thiophosphoryl chloride with silver cyanate in refluxing xylene was too slow to afford a practical method of preparation,[59] though there is evidence of the formation of the intermediate $Cl_2PS(NCO)$ from thiophosphoryl chloride and potassium cyanate.[66]

Thiophosphoryl *iso*cyanate is a colourless viscous liquid, b.p. 135°/30 mm., 215° (decomp.)/760 mm., refractive index for white light 1·5116, $d = 1{\cdot}538$ g./c.c. Other physical properties are given in Table I. Hydrolysis in nitric acid yields sulphur, claimed as evidence for a P=S group, rather than the isomeric P=O(SCN).[59]

### **Diphosphorus Tetra-*iso*cyanate** (Phosphorus Di-*iso*cyanate, $P_2(NCO)_4$)

Diphosphorus tetraiodide reacts with silver cyanate in an inert solvent, yielding diphosphorus tetra-*iso*cyanate, which closely resembles the tetracyanide (*q.v.*) in its physical and chemical properties. Infra-red absorption bands at 1420 and 763 cm.$^{-1}$ support the *iso*cyanate structure for this compound.[8]

## PHOSPHORUS THIOCYANATES AND *ISO*THIOCYANATES

### Phosphorus(III) *Iso*thiocyanate

Early attempts to prepare phosphorus(III) *iso*thiocyanate by reaction of phosphorus(III) chloride with silver or lead thiocyanate gave impure products,[15,70] but better results were obtained by conducting the reaction in the presence of charcoal to remove impurities which catalyzed decomposition.[33] The compound can also be made by the reaction of phosphorus(III) chloride with ammonium thiocyanate in boiling benzene,[3,71] mercurous thiocyanate in carbon tetrachloride[1] or potassium thiocyanate in liquid sulphur dioxide.[72,73]

Phosphorus(III) *iso*thiocyanate is a colourless highly refractive liquid, b.p. 87–8°C./0·08 mm.,[73] 118–20°C./1 mm.,[6] 163–168°C./15–17 mm. (decomp.),[71,74] f.p. −4°C., $d_4^{15} = 1{\cdot}483$ (see also Table III). The molecular refractivity (50·99,[6] 54·45 (recalc. from the data of ref. 74)) agrees more closely with the calculated value for $P(NCS)_3 = 52{\cdot}53$ than for $P(SCN)_3 = 57{\cdot}15$.[6] However, the crude material is said to contain two compounds, one of which dissolves much more readily in water than the other, giving thiocyanic and phosphorous acids. This has been claimed as evidence for the presence of some of the thiocyanate isomer.[71] Nevertheless, the infra-red and Raman spectra, which show strong bands at 1930 and 1050 cm.$^{-1}$, support the *iso*thiocyanate structure,[6,73] while the 7*a* and 9*e* fundamental vibrations observed accord with $C_{3v}$ symmetry, although it is not possible to determine whether the P–N=C=S groups are linear.[6]

If heated above 105° phosphorus *iso*thiocyanate polymerizes or decomposes to a black solid, and distillation above this temperature is always accompanied by considerable loss.[3] Even in sealed ampoules at room temperature in the absence of air, the substance darkens and deposits a brown polymeric solid.[1,73] Hydrolysis gives phosphorous acid and thiocyanic acid with smaller amounts of other phosphorus oxyacids and hydrogen sulphide[1,25] (see also page 472). Alcoholysis yields tri-(or di-)ethyl phosphite and thiocyanic acid with a trace of *iso*perthiocyanic acid[75]:

$$P(NCS)_3 + 3EtOH \rightarrow P(OEt)_3 + 3HSCN$$

$$3HSCN \xrightarrow{H^+} C_2H_2N_2S_3 + HCN$$

Aniline, even in excess, only gives a 1 : 1 adduct:

$$P(NCS)_3 + PhNH_2 \rightarrow PhNHCSNHP(NCS)_2$$

which reacts much more vigorously with water than does the parent *iso*thiocyanate.[3,74]

Sulphur dioxide oxidizes phosphorus *iso*thiocyanate to a mixture of phosphoryl and thiophosphoryl *iso*thiocyanates[76]:

$$3P(NCS)_3 + SO_2 \rightarrow SP(NCS)_3 + 2OP(NCS)_3$$

*Table III.—Physical Properties of the Phosphorus* Iso*thiocyanates*

| Compound | Boiling point °C.[a] | Freezing point °C. | Density (g./c.c.) | Constants in vapour pressure equation $\log p_{(\text{mm.})} = A - B/T$ | | Latent heat of vaporization kcal./mole | Trouton's constant g.-cal./deg.K. | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | $A$ | $B$ | | | |
| $P(NCS)_3$ | 163/15 mm. (decomp.) | | 1·487/15·5° | — | — | — | — | 71 |
| | 168/17 mm. | | 1·483/15° | | | | | 74 |
| | 141/0·3mm. (decomp.) | −4 | | | | | | 1 |
| | 118–20/1 mm. | | | | | | | 6 |
| | 87–8/0·08 mm. | | | | | | | 73 |
| $P(NCS)F_2$ | 90·3 | −95 | 1·452/20° | 7·7045 | 1752·9 | 8·08 | 22·2 | 9 |
| $P(NCS)Cl_2$ | 148 (decomp.) | −76 | 1·546/20° | ~9·427 | ~2757 | ~12·6 | ~29·9 | 33 |
| $PO(NCS)_3$ | 300 (extrap.)[b] | 13·8 | 1·484 | 8·5330 | 3240 | 14·82 | 25·8 | 50 |
| | 175/21 mm. | | 1·52/13·5° | | | | | 71 |
| | 159/11 mm. | | 1·518/15° | | | | | 74 |
| | 106–7/0·5 mm. | | | | | | | 73 |
| $PO(NCS)Cl_2$ | 173 | −55 | 1·587/25° | — | — | — | — | 49 |
| | 101/41 mm. | | | | | | | |
| $PO(NCS)_2F$ | 64–5/3·5 mm. | — | — | — | — | — | — | 52 |
| $PO(NCS)F_2$ | 35–6/87 mm. | — | — | — | — | — | — | 52 |
| $PS(NCS)_3$ | 121–3/0·3 mm. | — | — | — | — | — | — | 73 |
| | 124/0·1 mm. | — | — | — | — | — | — | 78 |
| $PS(NCS)_2F$ | 66–7/1·5 mm. | — | — | — | — | — | — | 52 |
| $PS(NCS)F_2$ | 85–90 | — | — | 7·715 | 1756·3 | 8·05 | 22·2 | 52 |

[a] At 760 mm. Hg unless stated otherwise.
[b] For other values see references 6, 78, 79.

**Refs. p. 594**

### Mixed Phosphorus(III) *Iso*thiocyanate Halides

Phosphorus(III) difluoride *iso*thiocyanate, $PF_2(NCS)$, has been made by the action of antimony(III) fluoride on phosphorus(III) *iso*thiocyanate. It is a colourless liquid, b.p. 90·3°C., m.p. −95°C., refractive index (white light, 20°) 1·4978, $d_4^{20}$ 1·452, molar refractivity 25·66 (see also Table III). It is infinitely miscible with carbon disulphide above −50°C. The chemical stability of the compound lies between that of $FP(NCO)_2$ and that of $F_2P(NCO)$.[9]

Mixtures of phosphorus(III) chloride or bromide and phosphorus(III) *iso*thiocyanate very rapidly undergo ligand exchange. Even at room temperature new nuclear magnetic resonance absorption lines show after a few minutes, and an equilibrium is reached in 12 hr., which is close to that expected for random reorganization. These results do not support the theory[77] that a non-linearity of chemical shifts in a series of mixed compounds is associated with a non-statistical ligand distribution. In these two cases the distribution is statistical, but the chemical shifts do not alter linearly (see Table IV).[10,38]

*Table IV.—Nuclear Magnetic Resonance Data on the Phosphorus* Iso*thiocyanates and Related Compounds*

| Compound | $^{31}$P N.M.R. spectrum | | | Ref. |
|---|---|---|---|---|
| | Coupling constant $J_{P-F}$, c.p.s. | Chemical shift $\delta_P$ p.p.m.$^{(a)}$ | Line intensity | |
| $P(NCS)_3$ | — | −85·6 | — | 38 |
| $P(NCS)_2Cl$ | — | −114·0 | — | 38 |
| $P(NCS)Cl_2$ | — | −155·3 | — | 38 |
| $PCl_3$ | — | −220·0 | — | 38 |
| $P(NCS)_2Br$ | — | −111·5 | — | 38 |
| $P(NCS)Br_2$ | — | −152·8 | — | 38 |
| $PBr_3$ | — | −229·0 | — | 38 |
| $OP(NCS)_3$ | — | +61·0 | — | 78 |
| | | 61·9 | — | 38 |
| $OP(NCS)_2F$ | 940 | 47·7 | 1:1 | 52 |
| $OP(NCS)F_2$ | 1016 | 36·4 | 1:2:1 | 52 |
| $OP(NCS)Cl$ | — | 41·5 | — | 78, 38 |
| $OP(NCS)Cl_2$ | — | 21·0 | — | 78, 38 |
| $OPCl_3$ | — | −2·2 | — | 38 |
| $SP(NCS)_3$ | — | +9·1 | — | 52 |
| | | 9·3 | — | 38 |
| | | 10·0 | — | 78 |
| $SP(NCS)_2F$ | 1060 | −12·2 | 1:1 | 52 |
| $SP(NCS)F_2$ | 1132 | +28·6 | 1:2:1 | 52 |
| $SP(NCS)_2Cl$ | — | −3·4 | — | 38 |
| $SP(NCS)Cl_2$ | — | −16·0 | — | 38 |
| $SPCl_3$ | — | −29·5 | — | 38 |
| $SP(NCS)_2Br$ | — | +28·4 | — | 78 |
| $SP(NCS)Br_2$ | — | 62·8 | — | 78 |
| $SPBr_3$ | — | 111·8 | — | 78 |

| Compound | $^{19}$F N.M.R. spectrum | | | Ref. |
|---|---|---|---|---|
| | Coupling constant $J_{F-P}$, c.p.s. | Chemical shift $\delta_F$ p.p.m.$^{(a)}$ | Line intensity | |
| $OP(NCS)_2F$ | 957 | +55·0 | 1:1 | 52 |
| $OP(NCS)F_2$ | 1012 | 71·6 | 1:1 | 52 |
| $SP(NCS)_2F$ | 1061 | 27·4 | 1:1 | 52 |
| $SP(NCS)F_2$ | 1123 | 36·6 | 1:1 | 52 |

(a) Reference compounds 85% $H_3PO_4$ or $CCl_3F$.

Because of rapid rearrangement it is difficult to isolate pure compounds in these series, but phosphorus dichloride *iso*thiocyanate has been reported to be a colourless liquid, b.p. 148°C. (decomp.), m.p. $-76$°C., $d_4^{20}$ 1·546, which hydrolyzes as rapidly as phosphorus trichloride.[33]

## Phosphoryl *Iso*thiocyanate

Phosphoryl *iso*thiocyanate is prepared by the action of phosphoryl chloride on lead thiocyanate in boiling cumene,[3,74] ammonium thiocyanate in benzene,[71] acetonitrile[73] or liquid sulphur dioxide,[78] silver thiocyanate in benzene,[50] or potassium thiocyanate in acetonitrile[72,73] or benzene.[79] After removal of the solvent, or in certain cases extraction of the residual solid with carbon tetrachloride, the crude phosphoryl *iso*thiocyanate is purified by distillation; b.p. 106–7°C./0·5 mm.[73], 145°/5–6 mm.,[79] 159°/11 mm.,[74] 300° (extrap.)/760 mm., m.p. 13·8°C.,[50] $d_4^{15} = 1{\cdot}518$ g./c.c., $n_D^{15} = 1{\cdot}6918$.[74]

Phosphoryl *iso*thiocyanate is a colourless liquid which decomposes to an orange[50] or black[3] polymer when heated above 250°. The molar refractivity (57·65,[6] 55·76 (calc. from the data of ref. 74)) agrees with that calculated for $OP(NCS)_3$ (58·45) rather than the value for $OP(SCN)_3$ (63·07). The infra-red and Raman spectra[6,73] support this, and are in accord with a $C_{3v}$ symmetry for the molecule.[6] Nuclear magnetic resonance data are given in Table IV.

The *iso*thiocyanate is rapidly and completely hydrolyzed by water[71] or 6N nitric acid[50]:

$$PO(NCS)_3 + 3H_2O \rightarrow 3HSCN + H_3PO_4$$

and gives a strong thiocyanate reaction with acidified iron(III) nitrate. It undergoes ligand exchange with mercury(II) chloride, benzoyl chloride, or dodecylsilicon trichloride[41]:

$$PO(NCS)_3 + 3PhCOCl \rightarrow POCl_3 + 3PhCO(NCS)$$
$$PO(NCS)_3 + HgCl_2 \rightarrow POCl_3 + Hg(NCS)_2$$
$$PO(NCS)_3 + C_{12}H_{24}SiCl_3 \rightarrow POCl_3 + C_{12}H_{24}Si(NCS)_3$$

and reacts with diamines to give polymers of unknown composition.[79]

## Mixed Phosphoryl *Iso*thiocyanate Halides

Phosphoryl difluoride *iso*thiocyanate is prepared by the action of difluorophosphoric anhydride on potassium thiocyanate[52]:

$$F_2P(O){-}O{-}POF_2 + KSCN \xrightarrow{25°C} F_2PO(NCS) + KPO_2F_2$$

Phosphoryl fluoride, thiocyanogen and polythiocyanogen are formed as by-products. Phosphoryl difluoride *iso*thiocyanate is a colourless liquid, b.p. 35–6°/87 mm. It disproportionates when heated, giving phosphoryl fluoride di-*iso*thiocyanate, b.p. 64–5°/3·5 mm. The infra-red and nuclear magnetic resonance spectra of the two substances have been recorded[52] (see also Table IV).

Phosphoryl chloride does not undergo ligand exchange with phosphoryl *iso*thiocyanate at room temperature during 1 week, but reacts after heating for several hours at 130–150°, reaching an equilibrium after 154 hr. which differs very little from that theoretically predicted for random distribution.[78] No physical properties except the nuclear magnetic resonance spectrum were recorded in this study. However, phosphoryl dichloride *iso*thiocyanate has been obtained in low yield by the reaction of phosphoryl chloride with silver thiocyanate[49] or potassium thiocyanate.[66] It is a colourless liquid, b.p. 101°/41 mm., 173°/760 mm., m.p. $-55$°C., $n^{20}$ 1·5649, $d^{25}$ 1·587, which shows significant disproportionation after 1 month at 25°C.[49]

**Refs. p. 594**

### Thiophosphoryl *Iso*thiocyanate

Thiophosphoryl chloride reacts with potassium thiocyanate in acetonitrile[72,73] or ammonium thiocyanate in liquid sulphur dioxide in an autoclave at 100°C.[78] to give thiophosphoryl *iso*thiocyanate, $SP(NCS)_3$. The same product is obtained in small yield by the oxidation of phosphorus(III) *iso*thiocyanate with sulphur dioxide[76]

$$3P(NCS)_3 + SO_2 \rightarrow SP(NCS)_3 + 2OP(NCS)_3$$

Thiophosphoryl *iso*thiocyanate is a liquid, b.p. 121–3°/0·3 mm.,[73] 124°/0·1 mm.[78] The nuclear magnetic resonance spectrum has been determined[78] (see Table IV).

### Mixed Thiophosphoryl *Iso*thiocyanate Halides

If thiophosphoryl *iso*thiocyanate is added dropwise to antimony(III) fluoride at 100°C. and 1–2 mm., a mixture of thiophosphoryl difluoride *iso*thiocyanate, b.p. 89·5–90°/760 mm., and thiophosphoryl fluoride di-*iso*thiocyanate, b.p. 66–7°/1·5 mm., is formed. Both are pale yellow liquids which darken in the presence of traces of water. The infra-red spectra have been recorded.[52] Other physical data are given in Tables III and IV.

Thiophosphoryl chloride or bromide reacts with thiophosphoryl *iso*thiocyanate only after prolonged heating.[38,78] Thiophosphoryl dichloride *iso*thiocyanate can be made by reaction of thiophosphoryl chloride with potassium thiocyanate. The nuclear magnetic resonance spectra are recorded (Table IV).

### Other *Iso*thiocyanates

Pyrophosphoryl *iso*thiocyanate has been obtained as a red involatile oil by the action of dry potassium thiocyanate on pyrophosphoryl chloride in acetonitrile.[80]

The reaction of phosphorus(V) chloride with mercurous thiocyanate yielded free dithiocyanogen, $(SCN)_2$, which rapidly polymerized. This suggests that phosphorus (V) *iso*thiocyanate is rather less stable than the corresponding iodide.[1]

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## SECTION XX

# THE REDUCED OXYACIDS OF PHOSPHORUS AND THEIR SALTS

BY H. A. J. CHAMP

In recent years several new oxyacids of phosphorus have been described in which one or more phosphorus atoms in the anion have an oxidation number of less than five.[23] This section will describe all the lower oxyacids of phosphorus apart from the three best known, hypophosphorous, phosphorous and hypophosphoric acids, which are discussed elsewhere.

The nomenclature of these reduced acids is rather confused at present, but the generally accepted names will be used in this section together with the shorthand nomenclature proposed by Blaser.[1] In this system the acid is designated by the phosphorus 'skeleton' of the anion, with a superscript figure which is the oxidation number of that particular phosphorus atom. Thus pyrophosphoric acid is represented by $P^5\text{–O–}P^5$ and hypophosphoric acid by $P^4\text{–}P^4$.

Although only three oxyacids of phosphorus containing only one phosphorus atom in the anion can exist, fourteen based on two phosphorus atoms could be postulated, and of these six are known: hypodiphosphorous, diphosphorous, hypophosphoric, pyrophosphorous, pyrophosphoric and isohypophosphoric acids. It is self-evident that with more phosphorus atoms in the anion the number of possible structures (including ring structures) would become legion and there is no obvious reason why many of these should not exist. In fact five acids based on three phosphorus atoms are already known.

The stabilities to hydrolysis and oxidation of these lower acids of phosphorus are briefly compared in Table I and the following general features may be noted. Firstly, acids containing phosphorus–phosphorus bonds only are more stable to hydrolysis than those containing oxygen-bridged phosphorus atoms, particularly under alkaline conditions. However, this stability decreases with increasing chain length.

Secondly, apart from the $(P^3)_6$ ring acid, only acids containing phosphorus–hydrogen links are oxidized by iodine. Finally the phosphorus–phosphorus bond is stabilized to bromine oxidation if either of the phosphorus atoms concerned is linked to a third phosphorus atom through an oxygen bridge.

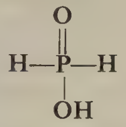
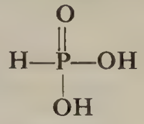
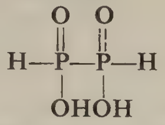
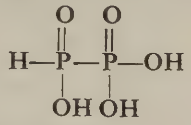
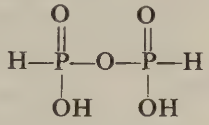
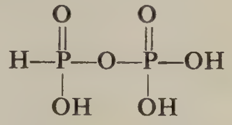
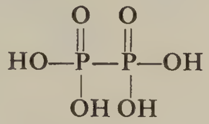
The properties of the acids and their salts will now be described in order of increasing molecular weight.

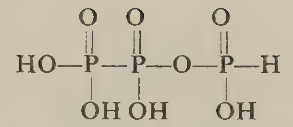
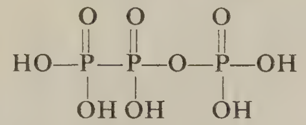
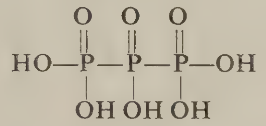
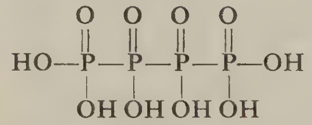
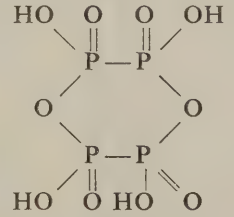
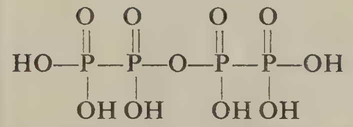
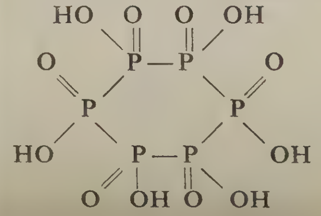
## HYPODIPHOSPHOROUS ACID, $P^2\text{–}P^2$ ACID, $H_4P_2O_4$

It has been claimed[2] that the anion of this acid is formed when diphosphorus tetraiodide is hydrolyzed in the presence of sodium bicarbonate. It is said to resist hydrolysis only in the region of pH 7·0 and to be oxidized by iodine in acid, neutral or alkaline solution. The product is diphosphorous or hypophosphoric acid, depending on the pH of the solution. The anion is also oxidized by atmospheric oxygen, and shows a tendency to disproportionate to phosphine and phosphorous or phosphoric acid.

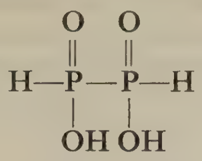
The barium salt is reported to be only sparingly soluble in 2 N. acetic acid (barium hypophosphite being soluble under these conditions), but no analytical details are given.

Table I.—The Stability towards Hydrolysis and Oxidation of Reduced Acids of Phosphorus

| Acid | Structural formula | Rate of hydrolysis in dilute | | Rate of oxidation at 25°C. | |
|---|---|---|---|---|---|
| | | acid | alkali | 0·1 N. $I_2/NaHCO_3$ | 0·1 N. $Br_2/NaHCO_3$ |
| Hypophosphorous<br>$P^1$ |  $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}H}$ | Decomposes on heating | | Very slow, but fast in acid | Slow |
| Phosphorous<br>$P^3$ |  $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}OH}$ | — | | 100% in 10 min. | 100% in 60 min. |
| Hypodiphosphorous<br>$P^2–P^2$ |  $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}H}$ | Very fast | Fast | Very fast | Fast |
| Diphosphorous<br>$P^2–P^4$ |  $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH}$ | Very fast | No change over 1 hr. in boiling N NaOH | Very fast | 100% in 15 min. |
| Pyrophosphorous<br>$P^3–O–P^3$ |  $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}H}$ | Very fast | Very fast | Stable | Very slow |
| Isohypophosphoric<br>$P^3–O–P^5$ |  $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH}$ | Half-life = 50 min. in 0·2 N. HCl at 0°C. | Half-life = 440 min. in 1·0 N. NaOH at 25°C. | Stable | Very slow |
| Hypophosphoric<br>$P^4–P^4$ |  $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH}$ | 100% in 1 hr. in 4 N. HCl at 100° | Stable | Stable | 100% in 15 min. |

| | | | | | |
|---|---|---|---|---|---|
| $P^4$–$P^4$–O–$P^3$ |  $HO-P(O)(OH)-P(O)(OH)-O-P(O)(OH)-H$ | Fast | Fast | Fast | Fast |
| $P^4$–$P^4$–O–$P^5$ |  $HO-P(O)(OH)-P(O)(OH)-O-P(O)(OH)-OH$ | Half-life = 95 min. in 0 8 N. $HNO_3$ | 5–10% hydrolysis on boiling for 1 hr. in 2–5 N. NaOH | Stable | Very slow |
| $P^4$–$P^3$–$P^4$ |  $HO-P(O)(OH)-P(O)(OH)-P(O)(OH)-OH$ | Slow | Very slow | Stable | Fast |
| $P^4$–$P^3$–$P^3$–$P^4$ |  $HO-P(O)(OH)-P(O)(OH)-P(O)(OH)-P(O)(OH)-OH$ | Fast | Slow | Stable | Fast |
| $(P^4$–$P^4$–$O)_2$ |  | Fast | Half-life = 138 min. in 0·28N. NaOH at 20°C. | Stable | Stable |
| $P^4$–$P^4$–O–$P^4$–$P^4$ |  $HO-P(O)(OH)-P(O)(OH)-O-P(O)(OH)-P(O)(OH)-OH$ | Fast | 100% in 2 hr. in 60% NaOH at 150°C. | Stable | Stable |
| $(P^3)_6$ ring acid |  | Fast | Fast | Fast | Fast |

The structure proposed from the chemical evidence is:



$$H-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-H$$

The relation of this form to the tautomeric $P_2(OH)_4$, postulated[3] as the first hydrolysis product of diphosphorus tetraiodide, would then be similar to that existing between the $HPO(OH)_2$ and $P(OH)_3$ forms of phosphorous acid.

The isolation of salts of hypodiphosphorous acid, with the exception of the barium salt mentioned above, does not appear to have been described.

## DIPHOSPHOROUS ACID, $P^2$–$P^4$ ACID, $H_4P_2O_5$

The presence of a previously unknown acid among the hydrolysis products of phosphorus trichloride was first suggested in 1935.[4] Further work confirmed the existence of an anion containing two directly bonded phosphorus atoms, though the free acid has not been described.

The trisodium salt is usually prepared by hydrolysis of phosphorus tribromide in neutral or weakly alkaline solution.[5,6,7]

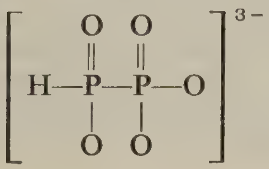
The sodium diphosphite, which is formed along with sodium phosphite, pyrophosphite and lesser amounts of phosphate and hypophosphate, is fractionally precipitated with alcohol and recrystallized from water. The main impurity is then hypophosphate which is removed as the sparingly soluble tetrasodium salt at pH 10–11, followed by further recrystallization of the diphosphite.

Phosphorus tribromide appears to give better yields of the diphosphite than does the trichloride.[8] Hydrolysis of diphosphorus tetraiodide and oxidation of $(P_4OH)_n$ with alkaline hypoiodite[37] give diphosphite, among other products.

Trisodium diphosphite crystallizes from water at 0°C. as the dodecahydrate, which is converted to a hexahydrate at 30°C. It becomes anhydrous on heating to 100°C. *in vacuo*[6,7]:

$$Na_3HP_2O_5,12H_2O \xrightarrow{30°C} Na_3HP_2O_5,6H_2O \xrightarrow[\textit{in vacuo}]{100°} Na_3HP_2O_5$$

Nuclear magnetic resonance[9] and Raman spectra[10] have shown that the structure of the anion is:



$$\left[H-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O\right]^{3-}$$

The nuclear magnetic resonance spectrum is complicated because of close spin–spin coupling between the hydrogen and the two interconnected phosphorus atoms. It is therefore necessary to apply a quantum mechanical treatment to the interpretation of the results. This is given elsewhere.[9,43] A typical spectrum is shown in Fig. 1.

The Raman spectrum of trisodium diphosphite shows intense lines at 2271 and 312 cm.$^{-1}$ which indicate P–H and P–P bonds respectively. The P–H line at 2271 cm.$^{-1}$ is however weaker than that shown by sodium pyrophosphite.[10]

The diphosphite anion is fairly stable to alkali but is readily hydrolyzed to phosphite in acid solution. The hydrolysis in 0·5 N. HCl at 20°C. has been shown to follow the equation:

$$K = \frac{1}{t}\ln\frac{C_A}{C_A - C_X}$$

where $K = 29{\cdot}2$–$30{\cdot}8 \times 10^{-3}$ min.$^{-1}$.[7]

**Refs. p. 612**

Sodium diphosphite is virtually unchanged after heating for 1 hr. with 2 N. sodium hydroxide solution and is only 60% decomposed after six hours' boiling with 30% NaOH. Higher concentrations of alkali and higher temperatures decompose the diphosphite more readily according to two equations[11]:

$$HP_2O_5^{3-} + H_2O \rightarrow 2HPO_3^{2-} + H^+$$

$$HP_2O_5^{3-} + H_2O \rightarrow P_2O_6^{4-} + H_2 + H^+$$

The second reaction predominates at higher alkali concentrations (83% in 80% NaOH and 60% in 40% NaOH).

The diphosphite anion is oxidized quantitatively by iodine to hypophosphate in 0·01 N. HCl. At higher acid concentrations the oxidation rate increases, but hydrolysis also occurs to a significant extent.[11] In bicarbonate-buffered solution iodine oxidizes diphosphite to hypophosphate, whereas chlorine and bromine oxidize it to pyrophosphate:

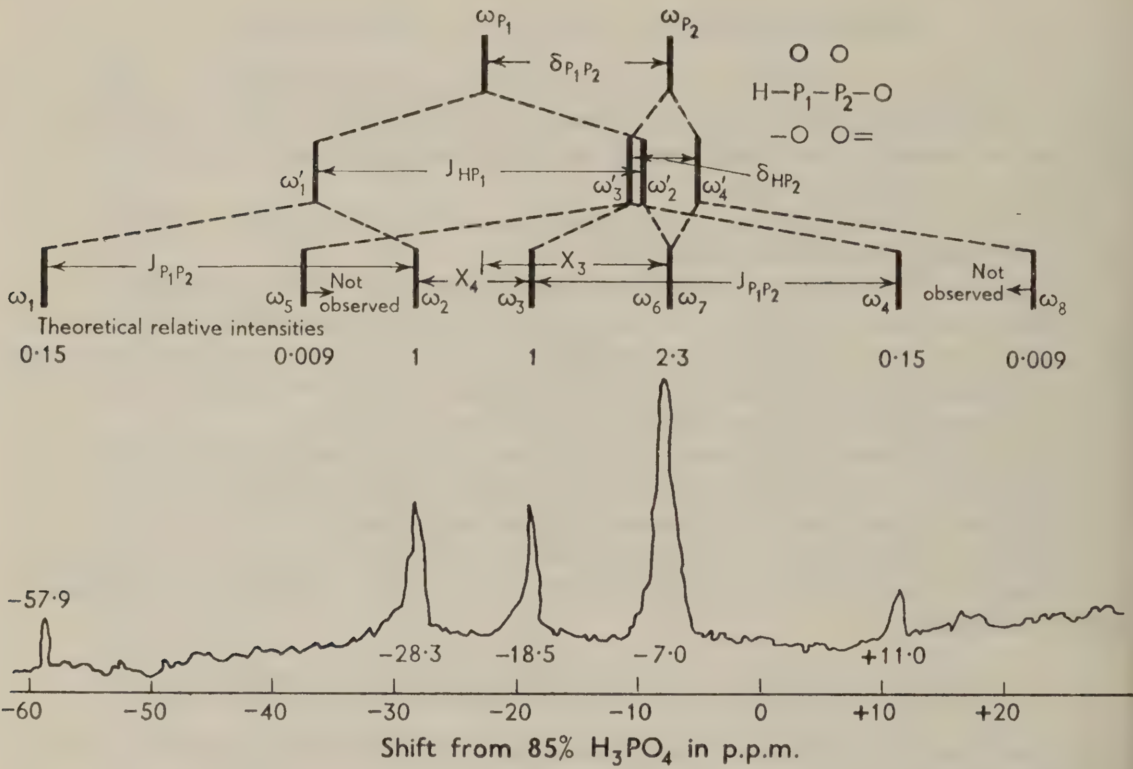


FIG. 1.—Zeeman levels and observed phosphorus spectrum for the diphosphite anion at a field of 9440 gauss. Because of saturation effects at the high r.f. field used to show up the small peaks, the peak areas are not strictly proportional to their predicted values. The measured values of $X_3$ and $X_4$ are 16·4 and 9·8 p.p.m. of the applied field as compared to the calculated values of 16·2 and 9·6 p.p.m., respectively. At the 7140 gauss field, the observed values of $X_3$ and $X_4$ are 21·9 and 9·5 p.p.m. compared to the calculated values of 21·6 and 10 p.p.m., respectively

$$HP_2O_5^{3-} + I_2 + H_2O \rightarrow P_2O_6^{4-} + 2I^- + 3H^+$$

$$HP_2O_5^{3-} + 2Br_2 + 2H_2O \rightarrow P_2O_7^{4-} + 4Br^- + 5H^+$$

## PYROPHOSPHOROUS ACID, $P^3$–O–$P^3$, $H_4P_2O_5$

Pyrophosphorous acid, which is isomeric with diphosphorous acid, and a few of its salts have been known since the late nineteenth century. The acid, however, was known only in the form of an unstable aqueous solution formed by the action of the stoicheiometric quantity of sulphuric acid on barium pyrophosphite. The pure acid has recently been prepared by reaction of phosphorus trichloride (or bromide) with phosphorous acid in the ratio of 1 : 5.[12–4] The product after removal of the halogen hydracid is claimed to have a purity of 99%.[12] It can be further purified by fractional crystallization from the melt. A closer study of the reaction shows that it is reversible:

$$5H_3PO_3 + PX_3 \rightleftharpoons 3H_4P_2O_5 + 3HX$$

Where phosphorus trichloride is used, the poor solubility of hydrogen chloride in the reaction mixture leads to a displacement of the equilibrium to the right, but in the case of phosphorus tribromide the reaction is both slower and less complete.[49] Earlier workers[15] claimed the formation of diphosphorus trioxide by this reaction.

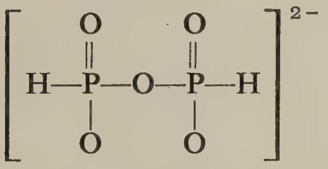
Pyrophosphorous acid is also formed during the thermal decomposition of phosphorous acid but itself undergoes further decomposition to form pyrophosphoric acid, metaphosphoric acid and phosphine.[17,49] Since these reactions occur to some extent simultaneously, this is not a practicable method of preparation:

$$2H_3PO_3 \rightarrow H_4P_2O_5 + H_2O$$

$$2H_4P_2O_5 \rightarrow H_4P_2O_7 + HPO_3 + PH_3$$

Under reduced pressure lower phosphorus hydrides, and even amorphous phosphorus, are formed, with a corresponding decrease in the yield of gaseous phosphine. Smaller quantities of pyrophosphorous acid also result from the hydrolysis of tetraphosphorus hexaoxide, or its reaction with phosphorous acid, and from the condensation of phosphorous acid by di*cyclo*hexylcarbodi-imide.[49] The P(III)(V) oxide $P_4O_{8\cdot13}$ also yields pyrophosphorous acid on hydrolysis.[50]

Nuclear magnetic resonance[9,12] and Raman spectra[14] of the acid and also the Raman spectrum of a saturated solution of the sodium salt[16] have shown that the structure of the anion is:



$$\left[\begin{array}{c} \mathrm{O} \quad\;\; \mathrm{O} \\ \| \qquad \| \\ \mathrm{H{-}P{-}O{-}P{-}H} \\ | \qquad | \\ \mathrm{O} \quad\;\; \mathrm{O} \end{array}\right]^{2-}$$

In the nuclear magnetic resonance spectrum two resonance peaks are observed at $-21$ p.p.m. and $+28$ p.p.m. (referred to the spectrum of 85% $H_3PO_4$ at 25°C.). The P–H splitting is 0·40 gauss, which is the same as that observed for phosphorous acid, and the chemical shift of 11 p.p.m. is approximately the same as that obtained in the change from phosphoric acid to pyrophosphoric acid.[12]

The Raman spectrum of the sodium salt[16] shows strong lines at 1107 $cm.^{-1}$ and 2412 $cm.^{-1}$ assignable to P–O–P and P–H vibrations respectively.

Melting points of 36°C.[12] and 39°C.[14] have been reported for pure pyrophosphorous acid.

Pyrophosphorous acid is stable to iodine in sodium bicarbonate buffered solution, but chlorine, under the same conditions, oxidizes pyrophosphorous acid to orthophosphoric acid (diphosphorous acid gives pyrophosphoric acid).[7]

Sodium pyrophosphite, $Na_2H_2P_2O_5$, is most conveniently prepared by heating monosodium phosphite at 110°–160°C. under reduced pressure[19,20]:

$$2NaH_2PO_3 \rightarrow Na_2H_2P_2O_5 + H_2O\uparrow$$

Under reduced pressure the pyrophosphite commences to decompose at about 225°C., decomposition being virtually complete by 350°C. when products are in approximately the following proportions: pyrophosphate 3%, phosphine 19%, tripolyphosphate 24% and trimetaphosphate 54%. At intermediate temperatures the ratios of the products formed differ from those quoted, and traces of orthophosphate and polyphosphates are found.[20]

Sodium phosphite reacts with phosphorus trichloride in an aqueous sodium bicarbonate buffered solution to give some sodium pyrophosphite. Hence pyrophosphite occurs among the hydrolysis products of phosphorus trichloride.[8]

Sodium pyrophosphite is also formed during the pyrolysis of disodium hypophosphate[22] and by heating disodium phosphite in a sealed tube at 180°C. for 1–2 hr. with iodine.[21] The latter reaction has been formulated as:

$$4Na_2HPO_3 + 2I_2 \rightarrow 4NaI + Na_2H_2P_2O_5 + Na_2H_2P_2O_7$$

Traces of a further unidentified species are also found.

The hydrolysis of the pyrophosphite ion is markedly dependent on the presence of other ions. Outside the range pH 5–8 it is rapidly hydrolyzed and this property is utilized analytically for the determination of mixtures of pyrophosphite and isohypophosphate. In 0·1 N. NaOH solution pyrophosphite is hydrolyzed to over 97% in half an hour, whereas isohypophosphate is decomposed to less than 1% in this time.[18, 47] The rate of hydrolysis is given by:

$$-R/[H_2P_2O_5^{2-}] = k_0 + \sum_a k_a[HA]_a + \sum_b k_b[B]_b$$

where $k_a$ and $k_b$ are catalytic coefficients, and $[HA]_a$ and $[B]_b$ are the concentrations of all Brönsted acids and Lewis bases respectively. The nuclear magnetic resonance spectra of partly hydrolyzed pyrophosphite solutions give evidence for the formation of intermediate species in the base catalyzed reaction.[51] The effects of some other ions on the hydrolysis are shown in Table II below.

*Table II.—Half-life of Pyrophosphite in* 0·05 *Molar Solution at* 30°C.

| Added salt | Concentration mole/litre | Half-life of pyrophosphite in hours |
|---|---|---|
| $NaHCO_3$ | 0·1 | 500 |
| | 1 | 24 |
| | 3 | 2 |
| $CH_3CO_2Na$ | 0·1 | 600 |
| | 1 | 70 |
| | 3 | 8 |
| $Na_2SO_4$ | 1 | 120 |
| $NaH_2PO_2$ | 1 | 110 |
| | 3 | 19 |
| NaCl | 1 | 250 |

There is some evidence to suggest that, in the presence of fluoride ions, pyrophosphite forms phosphite and a transient fluorophosphite which further decomposes to fluoride and more phosphite.

Pyrophosphite reacts with orthophosphate to form isohypophosphate in aqueous solution.[24–6, 47] This process has been termed interanhydrization. The reaction is dependent upon the phosphate concentration, high yields of isohypophosphate being favoured by high phosphate concentrations. The pH of the solution also affects the yield. Outside of the range pH 5–8 there is a marked fall in the isohypophosphate formed owing to hydrolysis of the pyrophosphite:

$$H_2P_2O_5^{2-} + PO_4^{3-} \rightarrow HPO_3^{2-} + HP_2O_6^{3-}$$

A similar reaction occurs between pyrophosphite and hypophosphate[24, 47] and possibly also between pyrophosphite and pyrophosphate[47]

$$H_2P_2O_5^{2-} + P_2O_6^{4-} \rightarrow HPO_3^{2-} + HP_3O_8^{4-} \qquad (P^4\text{—}P^4\text{—}O\text{—}P^3)$$

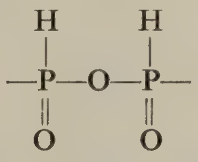
$$H_2P_2O_5^{2-} + P_2O_7^{4-} \rightarrow HPO_3^{2-} + HP_3O_9 \qquad (P^3\text{—}O\text{—}P^5\text{—}O\text{—}P^5)$$

Ammonium pyrophosphite has been prepared by heating monoammonium phosphite at 100–110°C. *in vacuo* over barium oxide. The product is a deliquescent, white solid which becomes yellow on prolonged heating above a temperature of 130°C.[27]

The hydrolysis of ammonium pyrophosphite has been shown to be similar to that of other pyrophosphites, i.e. it is slow at pH 5–7 but is very rapid outside the range pH 2–9.[28]

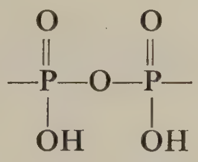
## HIGHER POLYPHOSPHOROUS ACIDS

No trace of polyphosphorous acids higher than pyrophosphorous could be detected by nuclear magnetic resonance spectroscopy or paper chromatography, either in molten pyrophosphorous acid, or in the products of other polycondensation reactions. Thus the reaction of phosphorous acid with excess of phosphorus trichloride, or the interaction of tetraphosphorus hexaoxide with phosphorous or pyrophosphorous acids, yielded only impure pyrophosphorous acid, together with some phosphate, and a yellow solid containing P–P and P–H bonds.[52] Similarly the thermal dehydration of a range of metal phosphites leads to coloured products of uncertain composition with lower oxidation equivalent. Very acid salts, such as $NaH_3(HPO_3)_2$, give pyrophosphite, but then lose phosphorous acid by volatilization.[53] This confirms that the theoretical arguments adduced[54] for the instability of polyphosphites are correct. It appears that the



$$-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{P}}-O-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{P}}-$$

grouping is not only more unstable to hydrolysis than pyrophosphate, but also disproportionates readily to –P–P– and

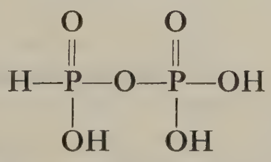


$$-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-$$

derivatives.[52]

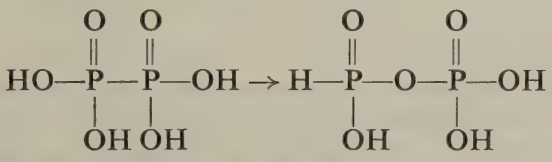
## ISOHYPOPHOSPHORIC ACID, $P^3$–O–$P^5$, $H_4P_2O_6$

In 1936 a study of the crystalline forms of hypophosphoric acid showed the presence of a hitherto unidentified species among their decomposition products. It was suggested[31] that this might be an isomer of hypophosphoric acid having the structure:



$$H-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$$

It was not until much later, however, that the sodium salt of isohypophosphoric acid was isolated from this source[29] and other workers confirmed that the isomerization does take place by following the decomposition by observation of the Raman spectra.[16, 30]



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH \rightarrow H-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$$

There is no evidence for the reverse reaction.

Further support for the structure has come from the nuclear magnetic resonance spectrum.[9] This is shown below in Fig. 2.

Isohypophosphoric acid is itself unstable and disproportionates to pyrophosphorous and pyrophosphoric acids.[16]

There are four main methods available for the preparation of sodium isohypophosphate, three of which depend on the condensation of phosphorous and phosphoric acids or their residues.

(1) Mixtures of phosphorous and phosphoric acids are carefully dehydrated under reduced pressure. The phosphoric acid may be partially dehydrated before the reaction is commenced, i.e. a higher polyphosphoric acid or a mixture of phosphoric acid and phosphorus pentoxide may be employed. The oil obtained is then neutralized by dropwise addition to a cooled solution of an excess of sodium bicarbonate.[18]

(2) Halogen compounds of pentavalent phosphorus are hydrolyzed in a solution of sodium phosphite, buffered by an excess of sodium bicarbonate. The reaction may also be performed by hydrolysis of a halide of trivalent phosphorus in a solution of an orthophosphate or by hydrolysis of a mixture of a trihalide and a pentahalide of phosphorus in a bicarbonate buffered solution. Either chlorides or bromides may be used and the hydrolysis is best performed with cooling in the range 0–5°C.[5,29,32-4,44]

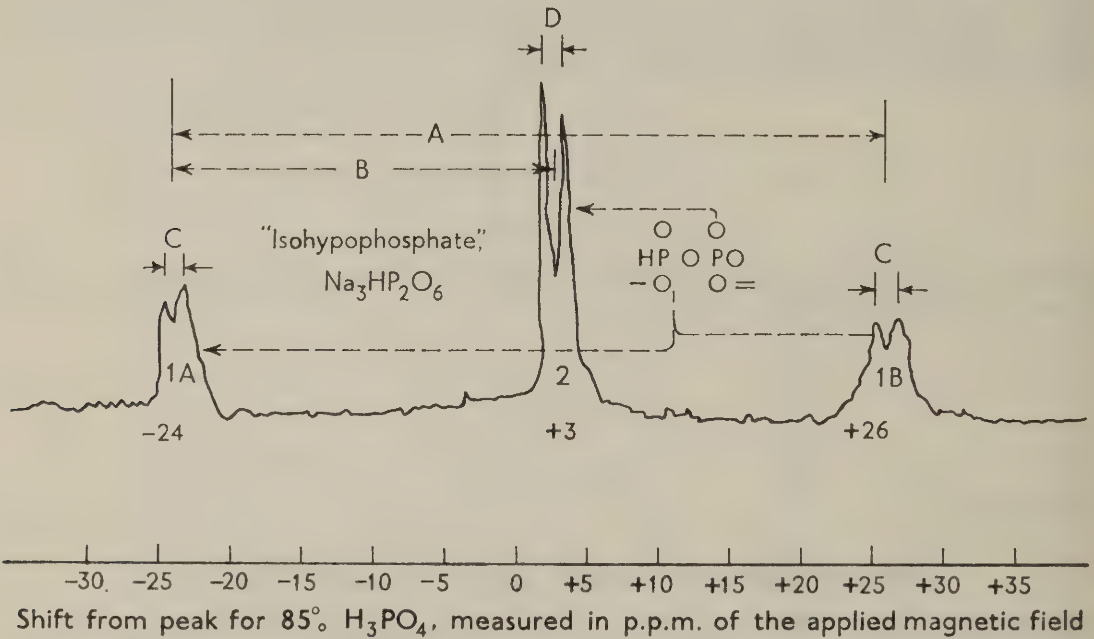


FIG. 2.—$^{31}$P magnetic resonance spectrum of the isohypophosphate anion at 7140 gauss and 12·3 Mc.: A = 620 c.p.s.; B = 27 p.p.m. or 328 c.p.s.; C = 17 c.p.s.; D = 17 c.p.s.

(3) Dehydration of a mixture of equivalent amounts of disodium orthophosphate and monosodium phosphite by heating *in vacuo* to constant weight at about 180°C. also gives a fair yield of anhydrous trisodium isohypophosphate.[26]

(4) High yields are claimed for a preparation depending upon interanhydrization between sodium pyrophosphite and disodium orthophosphate in neutral aqueous solution over a period of days[24-6,47]:

$$H_2P_2O_5^{2-} + PO_4^{3-} \rightarrow HP_2O_6^{3-} + HPO_3^{2-}$$

All the above reactions afford a mixture of salts containing, besides the isohypophosphate, phosphite, pyrophosphite, orthophosphate, pyrophosphate and sometimes lesser amounts of higher condensed phosphates. Separation depends on oxidation of the phosphite with iodine in bicarbonate-buffered solution after preferential hydrolysis of any pyrophosphite in weakly alkaline solution. The phosphates are removed by fractional precipitation with alcohol, the last few per cent. being preferentially precipitated as the lead salts.

The isohypophosphate anion has also been identified in small quantities when phosphorus trichloride or bromide is hydrolyzed in sodium bicarbonate buffered solution.[8]

Paper chromatography has been applied to the separation of the isohypophosphate anion, which in Thilo's ammoniacal solvent[8] has an $R_f$ value of 0·49–0·50.[26]

Trisodium isohypophosphate has been prepared anhydrous and also as octa- and tetrahydrates:

$$Na_3HP_2O_6{,}8H_2O \xrightarrow[\text{1 day}]{\text{in air}} Na_3HP_2O_6{,}4H_2O \xrightarrow[\textit{in vacuo}]{100^\circ C} Na_3HP_2O_6 \quad ^{29}$$

In addition to the nuclear magnetic resonance and Raman spectra mentioned earlier, *X*-ray powder photographs have been published for both hydrates. The anhydrous salt is said to be amorphous to *X*-rays.[29]

The salt is stable at room temperature in neutral aqueous solution but is hydrolyzed by both acid and alkali to a mixture of phosphite and orthophosphate. Hydrolysis is more rapid in acid solution, being virtually complete in 1 hr. in 0·1 N. $H_2SO_4$, whilst the half-life in 0·1 N. NaOH is given as 440 minutes at room temperature. The kinetics have been studied in 0·2 N. HCl at 0°C. and 1·0 N. NaOH at 34·2°C.; it was found that the values of the respective reaction constants $K$ were $1{\cdot}35–1{\cdot}43 \times 10^{-2}$ and $5{\cdot}39–5{\cdot}51 \times 10^{-3}$ min.$^{-1}$ where

$$K = \frac{1}{t} \ln \frac{C_A}{C_A - C_X} \quad ^{29}$$

Potentiometric titration shows two steps corresponding to the disodium and trisodium salts at pH 4·5 and pH 8·5, respectively. The disodium salt does not, however, appear to have been isolated.

The isohypophosphate anion is stable to iodine in the presence of sodium bicarbonate, but it is slowly and quantitatively oxidized to pyrophosphate by bromine under the same conditions.[29] Isohypophosphate, phosphite and pyrophosphite may be estimated iodometrically in the presence of one another. Only phosphite is attacked by iodine in the presence of sodium bicarbonate. Pyrophosphite is hydrolyzed to over 95% in 30 min. in 0·1 N. NaOH, whilst under these conditions the isohypophosphate anion is hardly affected:

$$H_2P_2O_5{}^{2-} + H_2O \rightarrow 2HPO_3{}^{2-} + 2H^+$$

The pyrophosphite may then be estimated by iodine oxidation of the phosphite liberated in this way. Hydrolysis in 0·1 N. mineral acid for 1 hr. converts isohypophosphate to phosphite and phosphate, after which it may be determined by an iodine oxidation of the liberated phosphite:

$$HP_2O_6{}^{3-} + H_2O \rightarrow PO_4{}^{3-} + HPO_3{}^{2-} + 2H^+$$

Alkaline earth and silver salts give colourless precipitates with solutions of sodium isohypophosphate. The precipitates consist of the tertiary salts but precipitation is not complete.[26, 29] The solubility of these salts, as might be expected from the structure of the anion, lies between those of the corresponding pyrophosphates and pyrophosphites.

The silver salt, which is white initially, darkens on standing. The lead salt, prepared by double decomposition between sodium isohypophosphate and lead acetate, hydrolyzes easily to phosphate and phosphite even in neutral solution.[26, 29] Lead pyrophosphite is similarly unstable.

## THE $P^4$–$P^3$–$P^4$ ACID, $H_5P_3O_8$

This acid was first observed among the products of oxidation by hypochlorite or hypobromite of red phosphorus in alkaline suspension, but may also be prepared by oxidation of both white and red phosphorus in acid solution.[38]

The acid itself has not been isolated in the pure state.

The highest yields of the pentasodium salt, $Na_5P_3O_8,14H_2O$, are obtained (up to 20%) by oxidation of the sodium potassium salt of the $(-P^3-)_6$ ring acid (*vide infra*) with iodine in the presence of sodium bicarbonate. Since the starting product itself can be obtained only in very small yield it is more convenient to prepare the sodium salt of the $P^4$–$P^3$–$P^4$ acid by oxidation of red phosphorus, either by hypochlorite or hypobromite in alkaline medium, or by hypochlorite or chlorite in acid solution. The main product of these oxidations is hypophosphate which is largely removed by crystallization of the reaction liquors at pH 10 after filtration of unreacted phosphorus. The traces of an anion containing four phosphorus atoms, which is probably the $P^4$–$P^3$–$P^3$–$P^4$ acid, are hydrolyzed much more rapidly than the $P^4$–$P^3$–$P^4$ acid and may be removed by making the solution approximately 0·3 N. with respect to hydrobromic acid and allowing the solution to stand for 1 hr. at room temperature. The $P^4$–$P^3$–$P^4$ acid and the remaining hypophosphate are separated from the other impurities, which are mainly phosphite and orthophosphate, by precipitation as their silver salts at pH 2·8. The silver salts are caused to react with sodium chloride and the hypophosphate and $P^4$–$P^3$–$P^4$ acid salt separated by fractional crystallization. This is possible since the pentasodium salt of the $P^4$–$P^3$–$P^4$ acid is soluble in its own weight of water at temperatures of 50°C. and above, whereas tetrasodium hypophosphate is only sparingly soluble. The yield of $Na_5P_3O_8,14H_2O$ is of the order of 2–3%.[35] This salt has also been isolated from phosphorus tribromide hydrolysates but only in yields of less than 1%. A further source of the $P^4$–$P^3$–$P^4$ acid is the polymer $(P_4OH)_n$ which can be oxidized by hypoiodite.[37]

When the lower phosphorus sulphides $P_4S_3$, $P_4S_5$ and $P_4S_7$ are hydrolyzed under alkaline conditions in the presence of hydrogen peroxide, the $P^4$–$P^3$–$P^4$ anion is formed together with phosphite, orthophosphate, pyrophosphate, hypophosphate and the $P^5$–O–$P^4$–$P^4$ anion.[45–6] Under the optimum conditions, the $P^4$–$P^3$–$P^4$ ion accounted for 15·5% of the phosphorus present. The yield increased in the order $P_4S_7 < P_4S_5 < P_4S_3$, other conditions being equal. Oxidative hydrolysis of diphosphorus tetraiodide gave a similar distribution of species. The hydrolysis of $P_2Cl_4$ or $P_2I_4$ in the absence of oxygen however, yields hypophosphite, phosphite, phosphate and (under basic conditions) diphosphine, but only traces of anions containing two or more phosphorus atoms.[58]

The salt obtained by crystallization from water is $Na_5P_3O_8,14H_2O$, which gives a unique *X*-ray powder photograph.[35] It may be converted to the anhydrous form by drying at 100°C. *in vacuo* over phosphorus pentoxide.

The $P^4$–$P^3$–$P^4$ acid is readily hydrolyzed by boiling with mineral acid to give phosphite and orthophosphate, but exhibits towards alkali a similar stability to that of other acids containing P–P bonds, i.e. diphosphorous acid and hypophosphoric acid. It shows very little decomposition even after boiling for several hours with 60% sodium hydroxide solution. The kinetics of hydrolysis in 1·5 N. nitric acid at 25°C. have been studied[35] and it was found that

$$K = \frac{1}{t}\ln\frac{C_A}{C_A - C_X} = 3{\cdot}09\times 10^{-3}\ \text{min.}^{-1}$$

so that the stability to acid hydrolysis lies between that of diphosphorous acid and that of hypophosphoric acid. Two mechanisms have been shown to be involved in the hydrolysis:

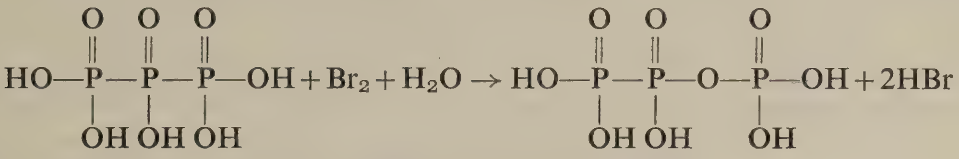
$$P_3O_8^{5-} + H_2O \rightarrow HPO_3^{2-} + P_2O_6^{4-} + H^+ \quad A$$

$$P_3O_8^{5-} + H_2O \rightarrow PO_4^{3-} + HP_2O_5^{3-} + H^+ \quad B$$

$$HP_2O_5^{3-} + H_2O \rightarrow 2HPO_3^{2-} + H^+ \quad C$$

Under the conditions of the above investigation, mechanism *A* occurred to the extent of 82% and mechanism *B*+*C* to 18%.

The $P^4$–$P^3$–$P^4$ acid is stable to halogens in acid solution and is stable to iodine in the presence of sodium bicarbonate over short periods, although considerable oxidation occurs over the period of a week. Bromine, in the presence of bicarbonate, oxidizes the $P^4$–$P^3$–$P^4$ acid quantitatively to the $P^4$–$P^4$–O–$P^5$ acid[35-6]:



$$\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH + Br_2 + H_2O \rightarrow HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH + 2HBr}$$

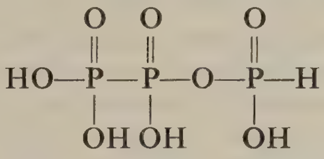
Potentiometric titration of the $P^4$–$P^3$–$P^4$ acid shows three steps, corresponding to the tri-, tetra- and penta-sodium salts. The trisodium salt, $Na_3H_2P_3O_8$,aq., has been prepared by adding acetic acid to a solution of the pentasodium salt and then precipitating the product with alcohol. The oil obtained is dissolved in water and reprecipitated with alcohol. It is finally dissolved in a little water which is allowed to evaporate spontaneously until the salt crystallizes.[35]

The silver salt is quantitatively precipitated from aqueous solution at pH 2·8 by the action of silver nitrate on the sodium salt. Even at this acidity, the pentasilver salt, $Ag_5P_3O_8$, is obtained as a white solid which slowly darkens on standing. It is slightly more soluble than the corresponding silver hypophosphate in the presence of phosphoric acid.

The sparingly soluble barium and magnesium salts have been prepared by double decomposition between the sodium salt of the $P^4$–$P^3$–$P^4$ acid and the alkaline earth halide. In the case of the barium salt, addition of barium hydroxide to pH 10·7 helps to prevent the formation of mixed salts.

### THE $P^4$–$P^4$–O–$P^3$ ACID, $H_5P_3O_8$

This acid, which is isomeric with the $P^4$–$P^3$–$P^4$ acid, and has the formula:



$$\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}H}$$

is known only in the form of its well-crystallized salts.[38,47] The sodium salt has been prepared by interanhydrization between disodium pyrophosphite and hypophosphate in neutral aqueous solution.[5,24,47] The reaction takes place either on boiling for a few minutes or on standing at room temperature over a period of days:

$$H_2P_2O_5{}^{2-} + P_2O_6{}^{4-} \rightarrow HP_3O_8{}^{4-} + HPO_3{}^{2-}$$

There is some evidence, mainly chromatographic, for an acid being present in very small quantities among phosphorus trihalide hydrolysates, and it is believed to have both P–P and P–O–P bonds in the anion. This may be the $P^4$–$P^4$–O–$P^3$ acid or the $P^4$–$P^4$–O–$P^5$ acid.[8,39]

The $P^4$–$P^4$–O–$P^3$ acid is itself capable of entering into interanhydrization reactions. When a neutral aqueous solution of a mixture of the sodium salts of the $P^4$–$P^4$–O–$P^3$ acid and orthophosphoric acid is allowed to stand, reaction takes place with production of hypophosphate and isohypophosphate[5]:

$$HP_3O_8{}^{4-} + PO_4{}^{3-} \rightarrow P_2O_6{}^{4-} + HP_2O_6{}^{3-}$$

The $P^4$–$P^4$–O–$P^3$ anion is hydrolyzed in both acid and alkaline solutions to hypophosphate and phosphite. The stability to alkali lies between that of pyrophosphite and isohypophosphate. The half-lives of the three species in 0·5 N. KOH solution at 0°C. are:

| | |
|---|---|
| Pyrophosphite | 1–1·5 min. |
| $P^3$–O–$P^4$–$P^4$ | 110 min. |
| Isohypophosphate | 3400 min.[47] |

It is oxidized by bromine in the presence of sodium bicarbonate to the $P^4$–$P^4$–O–$P^5$ anion[36]:

$$HP_3O_8^{4-} + HCO_3^- + Br_2 \rightarrow P_3O_9^{5-} + CO_2 + 2Br^- + 2H^+$$

but is stable to iodine.

## THE $P^4$–$P^4$–O–$P^5$ ACID, $H_5P_3O_9$

This acid may be regarded as an anhydride between orthophosphoric acid and hypophosphoric acid. Like the $P^4$–$P^4$–O–$P^3$ acid, it is known only in the form of its salts.

There are several methods of preparation available for the sodium salt but, unfortunately, those that give high yields depend on starting materials that are themselves difficult to prepare.[36, 38] Bromine in the presence of sodium bicarbonate as buffer oxidizes the $P^4$–$P^3$–$P^4$ acid and the $P^4$–$P^4$–O–$P^3$ acid quantitatively to the $P^4$–$P^4$–O–$P^5$ acid. Under the same conditions the $(P^3)_6$ ring acid is also oxidized to the $P^4$–$P^4$–O–$P^5$ acid, but in this case orthophosphate and pyrophosphate are also produced.

Hydrolysis of phosphorus oxychloride in a solution of an alkali hypophosphate, buffered by sodium bicarbonate, gives small yields of the $P^4$–$P^4$–O–$P^5$ acid. Hypophosphates may also be phosphorylated in concentrated aqueous solution by the action of monoamidophosphates at pH 4·5–8.[36, 38] It is claimed that yields of up to 25% may be obtained by this method.

This acid is also formed during the oxidative hydrolysis of the lower phosphorus sulphides.[45, 46] The highest yield (up to 16% of the total phosphorus present) was with the lowest sulphide ($P_4S_3$) under only mildly alkaline conditions. Diphosphorus tetraiodide behaved similarly to the sulphides.

Potentiometric titration has indicated the existence of tri-, tetra- and penta-sodium salts but, so far, only the last has been obtained as a solid, and it crystallizes with difficulty. It is hygroscopic and has been shown to be amorphous to *X*-rays.[36] The penta-ammonium salt is, however, obtainable in a crystalline form with slightly variable water of crystallization $(NH_4)_5P_3O_9$,*ca.* 1·2–1·6 $H_2O$.

The white silver salt is precipitated quantitatively in neutral solution by the action of silver nitrate on a solution of the sodium salt.[36]

The $P^4$–$P^4$–O–$P^5$ anion is stable to bromine and iodine in acid, neutral and alkaline solution. It is, however, unstable to hydrolysis although it is more stable to alkaline solutions than it is to acid. Boiling the $P^4$–$P^4$–O–$P^5$ acid with 2–5 N. NaOH causes 5–10% hydrolysis in an hour, whilst boiling with 60% alkali causes complete and rapid hydrolysis to orthophosphate and hypophosphate:

$$P_3O_9^{5-} + H_2O \rightarrow P_2O_6^{4-} + PO_4^{3-} + 2H^+$$

Boiling the acid with aqueous mineral acid hydrolyzes it to phosphorous acid and orthophosphoric acid in the ratio of 1 : 2:—

$$P_3O_9^{5-} + 2H_2O \rightarrow HPO_3^{2-} + 2PO_4^{3-} + 3H^+$$

The half-life in 0·8 N. nitric acid has been determined as 95 minutes ($K = 7{\cdot}34 \times 10^{-3}$ min.$^{-1}$).[36]

## THE $P^4$–$P^3$–$P^3$–$P^4$ ACID, $H_6P_4O_{10}$

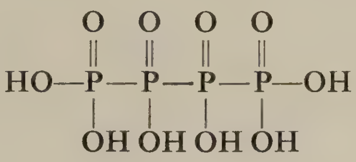
Although neither this acid nor any of its salts has yet been isolated, its existence has been postulated from chromatographic evidence.

It is believed to be formed in trace amounts during the oxidation of amorphous phosphorus by hypochlorite or hypobromite under alkaline conditions,[35] and also under some conditions during the degradation of the $(P^3)_6$ ring acid (*vide infra*).[40]

The anion, if it exists, is a homologue of the hypophosphate and $P^4$–$P^3$–$P^4$ anions and would be expected to show similar properties. As the $P^4$–$P^3$–$P^4$ acid is less stable to acid hydrolysis than hypophosphoric acid, so the $P^4$–$P^3$–$P^3$–$P^4$ acid would be expected to be still less stable and this appears to be true. If a solution containing the species believed to be the $P^4$–$P^3$–$P^3$–$P^4$ acid is made 0·3 N. with respect to hydrobromic acid, this species is completely destroyed in 2 hr., while much of the $P^4$–$P^3$–$P^4$ acid remains unchanged.[35] Similarly, by analogy with hypophosphoric acid and the $P^4$–$P^3$–$P^4$ acid, the $P^4$–$P^3$–$P^3$–$P^4$ acid would be expected to show considerable stability to alkali and have a silver salt insoluble at pH 2–8.

From chromatographic evidence for the decomposition of the $(P^3)_6$ ring acid, it appears that the $P^4$–$P^3$–$P^3$–$P^4$ anion is stable to iodine in acid and bicarbonate-buffered solution and to bromine in acid solution.[40] In this respect it is also exhibiting similar behaviour to that of its two homologues.

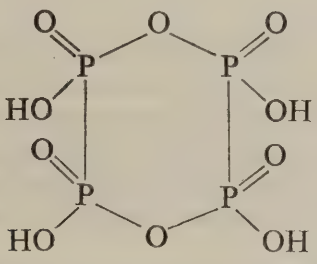
The structure of the acid would be:



$$\mathrm{HO}{-}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}{-}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}{-}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}{-}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}{-}\mathrm{OH}$$

## THE $(-P^4-P^4-O-)_2$ RING ACID

When tetrapotassium hypophosphate is treated with excess of acetic anhydride at 90°C. for periods up to 40 hr. it is converted to the salt of its cyclic anhydride acid $(-P^4-P^4-O)_2$[48]:



The product as obtained is amorphous but this can be converted to a tetraguanidinium salt which crystallizes readily in the form of a dihydrate. This can in turn be converted via metathetical reactions to the insoluble silver salt and finally to the sodium salt which crystallizes as a tetrahydrate. The barium salt is also insoluble.

Potentiometric titration shows only a single inflexion which is typical of the known cyclic phosphorus oxyacids.

The $(-P^4-P^4-O-)_2$ acid is readily hydrolyzed. When heated in the presence of mineral acids it decomposes, giving equimolecular amounts of orthophosphoric and phosphorous acids, but under strongly alkaline conditions (60% KOH at 150°) hypophosphate in the sole product. However under mildly alkaline conditions the ring is split across only one of the P–O–P bonds (*vide infra*).

The $(-P^4-P^4-O-)_2$ ring acid is stable to oxidation by iodine and bromine in the presence of sodium bicarbonate.

## THE $P^4$–$P^4$–O–$P^4$–$P^4$ ACID

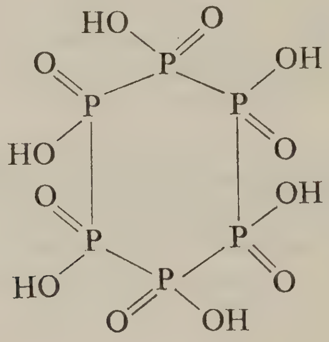
The anion of this acid is produced when the $(P^4-P^4-O)_2$ ring acid is hydrolyzed under mildly alkaline conditions (1·5 N. NaOH solution).[48] The sodium salt can be crystallized with approximately nine molecules of water of crystallization and is stable to oxidation by bromine in neutral solution. The potentiometric titration curve shows inflexions at pH 4·8–5·0 and pH 10·3 corresponding to the tetra- and hexa-sodium salts.

The acid is rather more stable to hydrolysis under alkaline conditions than the ring acid (e.g., 30 minutes reflux with 2 N. KOH solution only hydrolyzed 8·8% of a sample) but more vigorous conditions hydrolyze it completely to hypophosphate.

The insoluble silver and barium salts may be prepared from the sodium salt by metathetical reactions.

## THE $(P^3)_6$ RING ACID, $(HPO_2)_6$

It was found[5,38] that under alkaline conditions oxidation of amorphous phosphorus with either hypochlorite or hypobromite gave yields of up to 3% of a sparingly soluble sodium salt of a hitherto unknown oxyacid of phosphorus. This was identified as the salt of an acid containing six phosphorus atoms bonded in the form of a ring:



The free acid has not been prepared but several of the salts have been reported. If sodium ions are present during the oxidation of the phosphorus, the sparingly soluble sodium salt may be extracted with boiling water from the slurry of unreacted phosphorus at the end of the reaction. The potassium salt is more soluble but, such is the insolubility of the sodium salt, that even if the purest potassium salts available are used in the preparation the product obtained is usually found to contain up to 18 atom-% of sodium.[40-1]

The $(P^3)_6$ ring acid has also been prepared by oxidation of the polymer $(P_4OH)_n$ with an alkali metal hypoiodite.[37]

Three items of evidence suggest that the compound may have a ring structure. Firstly, analysis shows that the ratio of alkali metal to phosphorus is 1 : 1. Secondly, potentiometric titration shows only a single step and not a series of steps and, finally, the infra-red spectrum reveals no evidence for the presence of P–H bonds.

Crystallographic evidence has since confirmed that the anion is, indeed, cyclic in structure, the configuration being that of a buckled 6-membered ring of phosphorus atoms[42] (*vide infra*).

The pure sodium salt may be prepared from the crude product by recrystallization from an aqueous solution containing sodium bromide. The salt as crystallized contains 9·5–10·5 molecules of water per anion.

The pure potassium salt may be prepared from the mixed sodium potassium salt by first converting the latter to the thallium salt by double decomposition with thallous sulphate. The well-washed thallous salt is then suspended in water and treated with pure potassium iodide. After filtration of the precipitated thallous iodide, the pure potassium salt can be precipitated from the filtrate by alcohol and then recrystallized from water. The salt contains about 7·2 molecules of water for each anion.

The ammonium and cæsium salts have been prepared by a series of reactions similar to that which gives the potassium salt. The latter contains about 6·8 molecules of water for each anion.

The cæsium salt has been subjected to crystallographic investigation.[42] It crystallizes in the monoclinic system with $a = 9{\cdot}47$ A., $b = 9{\cdot}49$ A., $c = 16{\cdot}05$ A. and $\beta = 110{\cdot}5°$. The space group has been shown to be $C^5_{2h}$–$P2_1/C$ and there are two formula units to the unit cell. Figs. 3 and 4 show, respectively, a projection of the molecule onto the *ac*-plane and a three-dimensional representation of the anion.

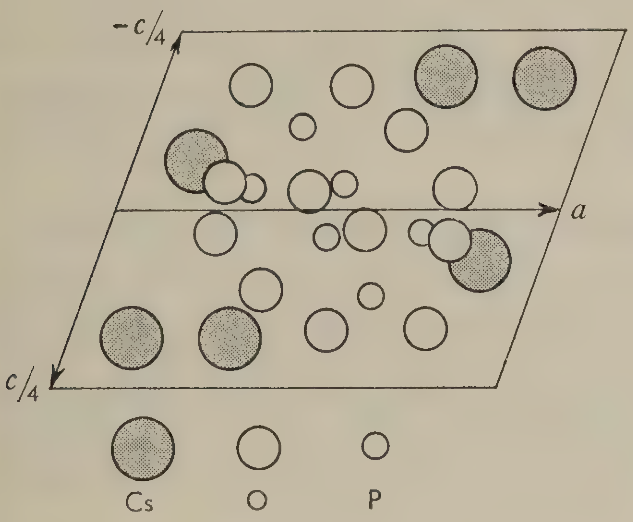


FIG. 3

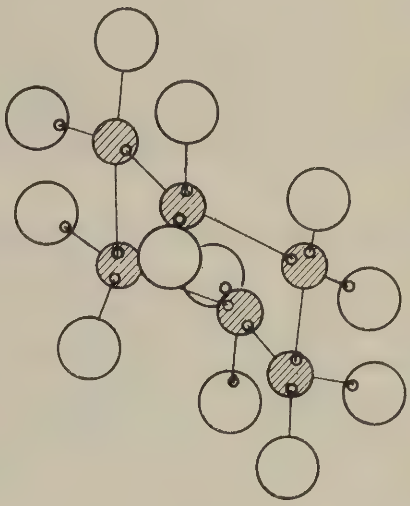


FIG. 4

Solubility measurements have been made[40] of the alkali metal salts, but the results are only approximate owing to the extreme sensitivity to the presence of even the slightest traces of sodium.

*Table III.—Solubility of Salts of the Acid* $(HPO_2)_6$

| Salt | Approximate solubility at room temperature (g. per 100 ml. $H_2O$) |
|---|---|
| $Cs_6P_6O_{12}$ | 170 |
| $K_6P_6O_{12}$ | 20 |
| $Na_6P_6O_{12}$ | 0·2 |
| $NaK_5P_6O_{12}$ (*ca.* 17 atom-% Na) | 2–2·5 |

The salts of the $(P^3)_6$ ring acid are readily hydrolyzed in acid and, unlike the other anions containing P–P bonds, also in alkaline solution. The hydrolysis is catalyzed by alkaline earth and heavy metal ions. For this reason, addition of gelatin to the suspension of amorphous phosphorus prior to oxidation increases the yield of the $(P^3)_6$ ring acid.

Acid hydrolysis yields mainly phosphorous acid with lesser amounts of hypophosphorous and orthophosphoric acid. Alkaline hydrolysis produces phosphorous and diphosphorous acids, although traces of hypophosphorous and hypophosphoric acids may also be formed. 50% sodium hydroxide at room temperature destroys the $(P^3)_6$ anion completely in 1 min., but with 1 N. or 2 N. NaOH the solution must be boiled to give the same result.

**Refs. p. 612**

The halogens oxidize the $(P^3)_6$ anion but the products formed vary according to the halogen used and the pH of the solution.

Iodine gives orthophosphoric, hypophosphoric, the $P^4-P^3-P^4$ and the $P^4-P^3-P^3-P^4$ acids. In acid solutions phosphorous acid is also found.

Bromine in the presence of sodium bicarbonate as buffer produces orthophosphate, pyrophosphate and the $P^4-P^4-O-P^5$ anion. There is also some chromatographic evidence that a species probably containing four phosphorus atoms per molecule is formed in traces. In acid media bromine gives orthophosphoric and hypophosphoric acids with traces of the $P^4-P^3-P^4$ and $P^4-P^3-P^3-P^4$ acids.[40]

Calcium, barium and magnesium halides all give precipitates with solutions containing the $(P^3)_6$ anion. The magnesium-containing compound has a Mg : P ratio of 1 : 2 and is probably the magnesium salt of the $(P^3)_6$ ring acid, but a zinc salt formed under similar conditions was shown to be partially hydrolyzed.

Silver nitrate also gives a colourless precipitate with an aqueous solution of the $(P^3)_6$ ring acid, but the precipitate rapidly darkens.

## THE ANALYSIS OF THE REDUCED OXYACIDS OF PHOSPHORUS

The lower oxyacids of phosphorus have been studied and separated primarily by paper chromatography.[8,26,55] A water–ammonia–methanol–dioxan solvent will separate all anions except $H_2PO_2^-/P^3-O-P^3$. A molybdenum spray reagent is used, with modifications for lower oxidation states.[55] Blue colours when obtained are due to $H_3PO_4$- heteropoly blue or $H_4P_2O_6$-heteropoly blue,[56] though $P^2-P^4$, $P^4-P^3-P^4$ and $(P^3)_6$ anions react with molybdate in acid solution to give a blue-green colour without any reducing agent.[57] The iodometric estimation of isohypophosphate–phosphite–pyrophosphite mixtures has been mentioned above.[29]

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### SECTION XXI

# HYPOPHOSPHOROUS ACID AND THE HYPOPHOSPHITES

### BY H. A. J. CHAMP

ALTHOUGH hypophosphorous acid and its salts have been known since the beginning of the nineteenth century[1] the alkaline hydrolysis of white phosphorus, first described a few years after the discovery of the acid, remains the only mode of preparation of any commercial importance. Calcium hydroxide is the base normally used, and it has been claimed that lower aliphatic alcohols catalyze the reaction.[2] It is also said to be advantageous to use a slight excess of phosphorus in the reaction.[2] A study of the solution of red phosphorus in aqueous potassium hydroxide at 100° showed that the maximum yield of hypophosphite is obtained at a concentration of 200 g. KOH/l. Higher concentrations of alkali yield more phosphite. Using sodium hydroxide at the same concentration, hypophosphite formation is favoured by increasing phosphorus concentrations. The reaction could be represented by the equation[178]:

$$4P + 4NaOH + 3H_2O \rightarrow 2NaH_2PO_2 + Na_2HPO_3 + PH_3 + H_2$$

The free acid may be prepared from a solution of the calcium salt by reaction with oxalic acid.[6] Hypophosphorous acid may also be conveniently prepared on the laboratory scale by the oxidation of phosphine in an aqueous solution of iodine.[5] This method avoids the possibility of explosions which occasionally occur during the usual preparation.

Phosphine is also oxidized to hypophosphorous acid by alkali hypochlorite solution and this reaction is utilized for scrubbing gases contaminated by phosphine:

$$PH_3 + 2NaOCl \rightarrow H_3PO_2 + 2NaCl$$

The kinetics of this reaction have been studied in the pH range 12–13. It was found that

$$-\mathrm{d}[NaOCl] / \mathrm{d}t = k[PH_3][NaOCl] / [OH^-]$$

where

$$k = 3{\cdot}47 \times 10^{10}\, e^{-12{,}200/RT}\ \mathrm{sec.}^{-1}$$

and the following reaction mechanism was postulated[165]:

$$\begin{array}{rll} OCl^- + H_3O^+ \rightleftharpoons & HOCl + H_2O & \text{(fast)} \\ PH_3 + HOCl \rightarrow & [PH_3O] + H^+ + Cl^- & \text{(rate determining)} \\ [PH_3O] + OCl^- \rightarrow & H_3PO_2 + Cl^- & \text{(very fast)} \end{array}$$

Hypophosphorous acid is also formed by oxidizing phosphine with iodine in weakly acid aqueous solution, though in strongly acid solution the reaction proceeds further to phosphorous acid.[210]

Hypophosphorous acid is also formed when lead phosphate is reduced with hydrogen at 350–399°C. and 250–298 atm. Colloidal lead oxide is produced at the same time. At higher temperatures (400°C. and over) and pressures (416 atm.) phosphine is also formed.[3–4] Some hypophosphorous acid is formed on mild oxidation of tetraphosphorous oxide ($P_4O$)[166] and on hydrolysis of the $(P^3)_6$ ring acid[167] but only as a by-product. Neither reaction is a practical method of preparation.

The main impurities in commercial hypophosphorous acid are phosphorous and phosphoric acids, which are generally removed as the sparingly soluble calcium salts. Any excess of calcium may then be removed in the form of some other insoluble salt, e.g. calcium oxalate. A method has been described whereby very pure hypophosphorous acid may be prepared from the commercial product (containing 2–3% of phosphorous acid as the main impurity) by evaporation and crystallization in an inert atmosphere followed by fractional melting, the solid at each stage being retained.[7]

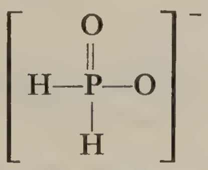
Early values for the melting point of hypophosphorous acid were 17·4°C. and 26·5°C.[3] Extrapolation of the water–hypophosphorous acid melting point diagram has given the value of $28{\cdot}8 \pm 0{\cdot}2$°C. for the melting point of the pure acid.[15] The same workers also determined the dissociation constant to be $5{\cdot}90 \times 10^{-2}$ from conductivity data measured at 25°C. and extrapolated to infinite dilution. A recalculation of Kolthoff's data[115] has given a value of $8{\cdot}0 \times 10^{-2}$ at 18°C.[149] Earlier workers in this field were Morton[16] and Bhagwat and Dhar.[17]

The results of a recent determination of the ionization constant of hypophosphorous acid are given in Table I.[161]

*Table I.—Ionization Constant of Hypophosphorous Acid*

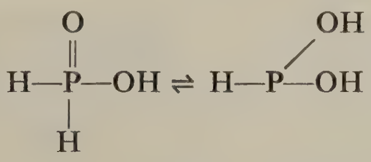
| Approximate ionic strength | Temperature °C. | Ionization constant $pK_1$ |
|---|---|---|
| 1·0 | 26·5 | 1·34 |
| 2·6 | 26 | 1·45 |
| 5·6 | 15·5 | 1·71 |

It is generally accepted[8–10] that the structure of the hypophosphite anion is



$$\left[\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}{-}O}\right]^-$$

although there is considerable evidence (*vide infra*) for tautomerism in the acid between the normal pentacovalent form and a tricovalent species:



$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}{-}OH} \rightleftharpoons \mathrm{H{-}\overset{\displaystyle OH}{P}{-}OH} \qquad \text{(‘active form’)}$$

From kinetic data on the oxidation of hypophosphorous acid by the halogens, it has been calculated that the equilibrium constant

$$K = \frac{[H_3PO_2 \text{ active}]}{[H_3PO_2 \text{ normal}]}$$

is of the order of $10^{-12}$.[163] The tautomeric change is said to have an activation energy of 18,200 g.-cal.[34] A comparison of the magnetic rotations and molar refractivities of esters $RP(OR)_2$ and $R_2P(O)OR$ with those of $H_3PO_2$ supports the $H_2P(O)OH$ structure for the latter.[179]

The Raman and infra-red spectra of the acid and its salts have been described by several workers.[9,72,125,150–5,168,180–3] Table II gives details of the frequencies observed for the potassium salt.

*Table II.—Raman and Infra-red Spectra of Potassium Hypophosphite*

| Frequency cm$^{-1}$ (approx.) | Infra-red spectrum | | | Raman spectrum | |
|---|---|---|---|---|---|
| | Aqueous solution | Crystalline salt | | Relative intensities | |
| | (Ref. 151) | (Ref. 155) | (Ref. 151) | (Ref. 151) | (Ref. 152) |
| 470 | (*m*) | — | (*m*) | 5 | 17 |
| 580 | — | — | — | — | 36 |
| 780 | — | — | — | — | 11 |
| 820 | (*s*) | 3 lines all (*s*) | (*s*) | 1 | 7 |
| 920 | — | — | — | 7 | 37 |
| 1050 | (*s*) | 3 lines all (*s*) | (*s*) | 10 | 100 |
| 1090 | (*m*) | (*s*) | (*w*) | 5 | 23 |
| 1160 | (*s*) | (*s*) | (*s*) | 7 | 33 |
| 1180–1230 | (*s*) | 4 lines (*s*), (*vs*) and 2 (*m*) | (*s*) | — | — |
| 1960 | — | (*vw*) | — | — | — |
| 2350 | (*w*) | (*s*) | (*m*) | 10 | 96 |
| 3400 | — | (*m*) | — | — | — |

(*s*) = strong, (*m*) = medium, (*w*) = weak.

From these spectra a non-planar $C_{2v}$ symmetry has been inferred, except possibly in the calcium salt where the symmetry appears to be $C_1$.[180]

The nuclear magnetic resonance spectra of hypophosphorous acid and some of its salts have also been studied[19,156–8] and again the results agree with those expected from the structure given above. Table III gives details of the $^{31}$P nuclear magnetic resonance spectra.[19]

*Table III.—Nuclear Magnetic Resonance Spectra of Hypophosphorous Acid and its Salts*

| Species | Chemical shift in p.p.m. relative to 85% $H_3PO_4$ | Line structure | Splitting in gauss |
|---|---|---|---|
| $H_3PO_2$ | $-13\pm2$ | 1–2–1 | 0·33 |
| $Ca(H_2PO_2)_2$ | $-8\pm2$ | 1–2–1 | 0·31 |
| $NaH_2PO_2$ | $-8\pm2$ | 1–2–1 | 0·31 |
| $KH_2PO_2$ | $-6\pm2$ | 1–2–1 | 0·31 |

Crystallographic examination of the hypophosphites of magnesium, nickel and cobalt has shown that the hypophosphite anion has a tetrahedral configuration.[122] From this work, the P–O bond distance was found to be 1·52 A. and the angle between the P–O bonds 109°. Similar investigations of ammonium hypophosphite give the P–O and P–H bond distances as 1·51 A. and 1·5 A. respectively,[124] whilst the angle between the P–O bonds is stated to be 120° and that between the P–H bonds to be 92°.

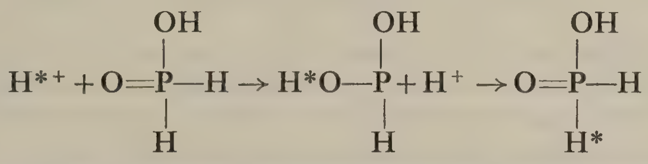
It has been observed that there is no exchange of phosphorus between hypophosphorous acid and either phosphorous or phosphoric acid in aqueous solution even in the presence of iodine.[11, 20, 39] There is, however, some exchange of oxygen in the free acid[21] and ready exchange of hydrogen for deuterium or tritium in acid, aqueous solution.[12–4, 22, 75, 169] There is no exchange of hydrogen in aqueous solutions of the hypophosphites unless free acid is present.[13–4, 22, 40]

The exchange of oxygen is thought to occur by addition of water to the P=O link forming $H_2P(OH)_3$.[21] The exchange has been shown to follow the equation:

$$-\ln(1-Z) = k(C_0+C_1)t$$

where $C_0$ and $C_1$ are the concentrations of water and acid respectively, $Z=y/y_\infty$ where $y$ = the excess of heavy oxygen and $y_\infty$ its content at equilibrium. The half-time of exchange at 40°C. is under 12 minutes.[21]

It is believed that the exchange of hydrogen occurs by addition of $H^+$ to the polar oxygen atom with simultaneous loss of $H^+$ from one of the P–H linkages followed by rearrangement, i.e.

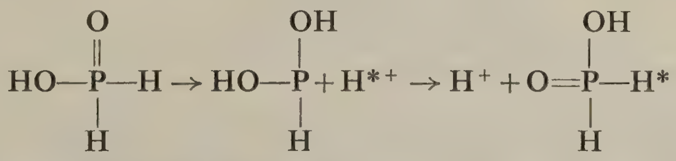


$$H^{*+} + O{=}\underset{H}{\overset{OH}{P}}{-}H \rightarrow H^{*}O{-}\underset{H}{\overset{OH}{P}} + H^{+} \rightarrow O{=}\underset{H^{*}}{\overset{OH}{P}}{-}H$$

The half-time of exchange at 25°C. is 16 min.[13] With no other acid present, the rate law is

$$R = k_{H^+}[H^+][H_3PO_2] + k_{H_3PO_2}[H_3PO_2]^2$$

At 30°C., $k_{H^+} = 3{\cdot}3 \pm 0{\cdot}15$ and $k_{H_3PO_2} = 2{\cdot}9 \pm 0{\cdot}14$.[12] It is possible that the tautomeric change occurs first, i.e.



$$HO{-}\underset{H}{\overset{O}{\overset{\|}{P}}}{-}H \rightarrow HO{-}\underset{H}{\overset{OH}{P}} + H^{*+} \rightarrow H^{+} + O{=}\underset{H}{\overset{OH}{P}}{-}H^{*}$$

The protonation of $H_2PO(OH)$ and $HPO(OH)_2$ in aqueous sulphuric acid has been studied by proton magnetic resonance. Calculations based on the variation of the P–H coupling constant with acid concentration did not yield $pK_a$ values consistent with the scales of Hammett function derived for other types of base. The results could best be interpreted in terms of a two-stage protonation:

$$H{-}O{-}H\cdots O{=}PH_n(OH)_{3-n} \xrightarrow{H^+} H_2O^+{-}H\cdots O{=}PH_n(OH)_{3-n}$$

$$\xrightarrow{H^+} H_3O^+ + H_nP(OH)^{+}_{4-n}$$ [211]

The oxidation of hypophosphorous acid by some oxidants (e.g. the halogens) obeys the same rate law and the catalytic coefficients are of the same order. Hence the two reactions probably follow a similar mechanism and provide support for the theory of tautomerism in hypophosphorous acid. There is also some evidence for dibasic character in the acid from conductivity data for the sodium salt.[18]

Hypophosphorous acid and the hypophosphites are very readily oxidized and many of their reactions involve oxidation–reduction processes. Although the oxidation potential of hypophosphorous acid does not seem to have been determined experimentally, the following values have been calculated[123]:

Under acid conditions,

$$H_2O + H_3PO_2 = H_3PO_3 + 2H^+ + 2e \qquad E^\circ = 0{\cdot}50 \text{ volts}$$

Under basic conditions,

$$3OH^- + H_2PO_2^- = HPO_3^{2-} + 2H_2O + 2e \qquad E^\circ_B = 1{\cdot}57 \text{ volts}$$

Hypophosphorous acid and also its salts undergo oxidation in aqueous solution, although some authorities state that catalysts must be present.[23] This oxidation may be inhibited by compounds with redox properties, such as hydroquinone.[24]

The free energies of disproportionation of hypophosphorous acid and of its oxidation by water have been stated to be[123]:

$$3H_3PO_2 \rightarrow PH_3 + 2H_3PO_3 \qquad \Delta F^\circ = -29{\cdot}9 \text{ kcal./ mole}$$

and

$$H_3PO_2 + H_2O \rightarrow H_3PO_3 + H_2 \qquad \Delta F^\circ = -23{\cdot}0 \text{ kcal./ mole}$$

The oxidation of hypophosphorous acid by atmospheric oxygen may be initiated by ozone or fluorine dioxide and a chain mechanism has been proposed for the reaction[25]:

$$HPO_2^- + O_2 \rightarrow HPO_4^-; \qquad HPO_4^- + H_2PO_2^- \rightarrow H_2PO_4^- + HPO_2^-$$

This reaction is accelerated by decrease in pH, increase in concentration, increase in temperature and by small amounts of heavy metal salts, although larger concentrations tend to inhibit the oxidation.[25] The order of reaction and the temperature coefficient of the rate of oxidation have been determined over the temperature range 20–40°. The activation energy of the reaction is 17·8 kcal./mole.[184]

Metallic palladium, copper, cobalt and nickel catalyze the aqueous oxidation of hypophosphorous acid and it has been suggested that under these conditions the first stage is the loss of hydrogen, followed by the addition of water.[27–8] However, isotope studies have shown that, of the hydrogen evolved in neutral solution, half is derived from the hypophosphite and half from the water.[27] A possible mechanism is:

$$\begin{aligned}&H_3PO_2 \rightarrow [H_2PO_2] + H\cdot\\&[H_2PO_2] + H_2O \rightarrow H_3PO_3 + H\cdot\\&2H\cdot \rightarrow H_2\end{aligned}$$

In the anodic oxidation of hypophosphorous acid on a palladium plated gold anode, the rate determining step is claimed to be the electrochemical ionization of the atomic hydrogen arising from a catalytic dehydrogenation such as that shown above.[185] It has been claimed, in fact, that hypophosphite is oxidized only at palladium anodes[186] although other authors have observed the formation of phosphite, phosphate and pyrophosphate at lead or copper anodes.[187] Cathodic reduction led only to phosphine formation.[187]

Hypophosphorous acid is quantitatively oxidized by iodine to phosphorous acid under acid conditions.[29–33] The most probable mechanism is that both the normal and active forms of hypophosphorous acid are in equilibrium with hypophosphite and $H_3PO_2.H^+$ ions. The iodine reacts with the hypophosphite ion and the active form of the acid. The latter reaction is subject to a general acid–base catalysis and the catalytic coefficients have been determined for several acids.[32] The same work claims that the transformation to the active form of hypophosphorous acid requires an activation energy $E_{k_1^\circ}$ of 20,000 g.-cal. and that for the reaction of iodine with the acid at 30°C. the catalytic coefficients are $k_1^\circ = 0{\cdot}35$ min.$^{-1}$ and $k_1^{H_3PO_2} = 0{\cdot}13$ min.$^{-1}$

The acid is oxidized by bromine and chlorine,[33–4, 38] the reaction being similar to that with iodine. Iodine monochloride and iodine trichloride also oxidize hypophosphorous acid.[35]

Chloramine reacts slowly but quantitatively with hypophosphorous acid in the presence of 0·24 N. sulphuric acid to form phosphorous acid.[36] It is said that in the presence of two equivalents of acetic acid the oxidation proceeds further to phosphoric acid.[37]

Iodic acid and the alkali metal iodates oxidize hypophosphorous acid to phosphorous acid, but it is not practicable to use this reaction for the quantitative analysis of hypophosphites, because of considerable interference from the iodate–iodide and iodine–phosphorous acid reactions.[41–3] There is also a considerable induction period which can be affected by temperature, concentration of the reactants and the presence of other species.[44] Both bromates and chlorates react similarly, again after an induction period,[45–6] though the chlorates oxidize hypophosphorous acid only in fairly concentrated solution. Bromate, or rather bromine monochloride formed *in situ* therefrom, has been used for the determination of hypophosphorous acid.[45]

When hypophosphorous acid is oxidized by hydrogen peroxide,[8] addition of ferrous ions increases the initial oxidation rate, although after this, the rate is the same whether ferrous or ferric ions are present.[47] Cuprous ions do not have this effect. Dihydroxymaleic, dihydroxytartaric and thioglycollic acids increase the activation by ferrous ions; this is believed to be due to some form of complex formation between the ferrous ion and the hypophosphorous acid, which renders the latter more readily oxidizable.[47]

Hydrochloric acid solutions of the arsenates are reduced by hypophosphorous acid to arsenic according to a second-order reaction[48–9, 148]:

$$\frac{-\mathrm{d}C_{\mathrm{As(OH)_3}}}{\mathrm{d}t} = KC_{\mathrm{As(OH)_3}}C_{\mathrm{H_3PO_2}} = KC_{\mathrm{As(OH)_3}}(B-(C_0-C))$$

where $B$ and $C_0$ are the initial concentrations of the hypophosphorous and arsenic acids respectively and $C$ is the concentration of the latter at time $t$. The velocity coefficients of the reaction vary with the initial concentrations of the reactants[49] and addition of potassium iodide accelerates the reaction.[129] The arsenic contains a little phosphorus (0·5–2%), the phosphorus content rising with increasing hypophosphite concentration and decreasing temperature.[188]

Some anomalous results were obtained when mixtures of arsenates and methylarsonates were reduced together. Highly coloured precipitates were formed instead of the expected brown mixture of arsenic and methylarsine. From mixtures rich in organic arsenate a yellow precipitate was obtained which was partially soluble in carbon disulphide, leaving a residue of arsenic. The solution slowly deposited more arsenic, eventually becoming colourless and containing methylarsine oxide.[48]

The kinetics of the reduction of arsenic trihalides by hypophosphorous acid have been studied and show that the rate of reaction decreases in the order $AsI_3 > AsBr_3 > AsCl_3$.[48]

When phosphorus or phosphine is oxidized by nitric acid under mild conditions, considerable quantities of hypophosphorous acid are formed, although hot nitric acid oxidizes it completely to phosphoric acid.[50]

Sulphuric acid is reduced by hypophosphorous acid in the presence of hydrogen iodide and this reaction has been developed into a method for the quantitative determination of sulphur in steel.[53] The seleninic acids are also reduced by hypophosphorous acid in dilute hydrochloric acid solution. The products are either seleninous acids or selenides depending on the reaction conditions.[51]

Ferricyanides are reduced by hypophosphites in alkaline solution and osmium tetroxide is said to catalyse the reaction.[52]

Hypophosphorous acid also reduces solutions of many of the heavy metals although under carefully controlled conditions the hypophosphites of some of the metals, which are normally reduced, may be prepared. Silver, gold and under some conditions copper, mercury and palladium, are reduced to the metal. The reaction has been proposed as a method of gravimetric analysis for all these metals except copper,[54–6] although some workers have used the reduction of mercuric salts to mercurous chloride by hypophosphorous acid as a method of analysis.[57–8, 127]

The complex of mercury with ethylenediamine tetraacetic acid (EDTA) is reduced to the metal and EDTA and this has been utilized as an indirect method of determining hypophosphorous acid.[170]

The kinetics of the reduction of cupric salts by hypophosphorous acid have been studied[60–1] and it has been proposed that copper hypophosphite may be formed as an intermediate product, which then decomposes under the reaction conditions. A moderately stable solution of copper hypophosphite has been prepared by some investigators.[61] It decomposes at 70°C. to form the unstable copper hydride CuH and reacts with cupric chloride to give cuprous chloride. Other workers have also obtained copper hydride by reduction of copper sulphate with hypophosphorous acid at 50–55°C. in an atmosphere of hydrogen.[26] For the reduction to copper metal according to the reaction:

$$2CuSO_4+2H_2O+H_3PO_2 \rightarrow 2Cu+2H_2SO_4+H_3PO_4$$

the empirical equation $C=at^{-m}$ has been deduced from kinetic data measured at 47°C. In the equation, $C$ is the concentration of cupric ions, $t$ is the time of reaction, and $a$ and $m$ are constants. This equation reduces to $\log C=2{\cdot}2932-0{\cdot}48 \log t$.[60]

Although some investigators have observed the formation of hydrogen when silver salts are reduced by hypophosphorous acid,[159] more recent studies failed to confirm this when equimolar concentrations of the reactants were mixed under a wide range of conditions.[59] The later workers suggest that silver hypophosphite first formed then decomposes to form silver and hypophosphite radicals. The latter react with water to form hypophosphorous acid and oxygen, which then oxidizes the acid to phosphorous and phosphoric acids.

The reduction of mercuric salts has been shown to involve four reactions[62]:

$$\begin{aligned}
&(1)\ 2Hg^{++}+H_2PO_2^-+H_2O \rightarrow Hg_2^{++}+H_2PO_3^-+2H^+\\
&(2)\ Hg_2^{++}+H_3PO_2+H_2O \rightarrow 2Hg^\circ+H_3PO_3+2H^+\\
&(3)\ Hg^\circ+Hg^{++} \rightarrow Hg_2^{++}\\
&(4)\ H_3PO_3+2Hg^{++}+H_2O \rightarrow Hg_2^{++}+H_3PO_4+2H^+
\end{aligned}$$

In the presence of chloride ions a fifth reaction takes place:

$$(5)\ Hg_2^{++}+2Cl^- \rightarrow Hg_2Cl_2\downarrow$$

Reaction (1) is the main rate-controlling reaction and the velocity constant for this step is given as $k=11{\cdot}42$ min.$^{-1}$ at 25°C. and $1{\cdot}42$ min.$^{-1}$ at 0°C. From these figures an activation energy of 13,600 g.-cal. has been derived.

Reaction (2) is believed to involve a preliminary tautomeric change in the hypophosphorous acid similar to that occurring in the exchange of hydrogen and oxidation by iodine.

Reaction (3) is so rapid that no mercury metal appears until after the removal of all the mercuric ions from the system.

Reaction (4) makes a significant contribution to the rate of removal of mercuric ions towards the middle of the overall reaction.

Germanium(IV) compounds are reduced to germanium(II) by hypophosphorous acid, or even further depending on the conditions.[63, 148] The reduction of uranyl sulphate is photocatalyzed and yields a mixture of products including hypophosphite, phosphite and phosphate with uranous sulphate.[64]

The reduction of cerium(IV) by hypophosphite may be utilized for the determination of the latter.[171] The rate of the reaction is about 1/200 of that which would be expected from strong acid catalysis theory, and the mechanism appears to involve Ce(IV) complex ions, as suggested by the rate expression[189]:

$$-\tfrac{1}{2}\mathrm{d}[\mathrm{Ce(IV)}]/\mathrm{d}t = [H^+]_{n=1}^{n=3} kH_n^+[Ce(H_2PO_2)_n^{(4-n)+}]$$

Bismuth salts are also reduced, usually to the metal, although bismuth hypophosphites may be formed as unstable intermediates.[65–6] An empirical equation has been derived for this reaction at 50°C.:

$$\log C = -2{\cdot}523-0{\cdot}10 \log t$$

where $C$ is the concentration of bismuth and $t$ is the time of reaction.[66]

The kinetics of the reaction between hypophosphorous acid and dichromate ion in sulphuric acid have been studied and show that the reaction is first order with respect to hypophosphorous acid and second order with respect to dichromate. The following mechanism was proposed[172]:

$$H_3PO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_3PO_2 \qquad \text{(active form)}$$

$$H_3PO_2\ \text{(active form)} + H^+ + 2HCrO_4 \xrightarrow{-k_3} H_3PO_3 + HCr_2O_6^- + H_2O$$

where $HCr_2O_6^-$ rapidly reduces to Cr(III).

$$\frac{k_1k_3}{k_2} = 466\ \text{sec.}^{-1}\ \text{at}\ 25°\text{C.}$$

A Mn(III) phosphate, prepared from Mn(IV) and Mn(II) in phosphoric–sulphuric acid solution, quantitatively oxidizes hypophosphite to phosphate.[190]

Molybdic acid and tungstic acid sols are reduced by hypophosphorous acid, the reaction involving photochemical initiation.[90] The reaction is complex and the velocity constant is said to depend on the temperature, reactant concentrations, pH of the medium and even the polarization of the incident light, although not all these factors apply to both reactions.

Hypophosphorous acid also reduces aryl diazonium salts. Investigations using hypophosphorous acid labelled with deuterium have shown that the mechanism involves the transfer of a hydrogen from a P–H bond to the aromatic nucleus.[67–9] The yield in this reaction is improved by the addition of copper sulphate or, in the case of certain aryl groups, ferrous sulphate.[70]

The reaction of hypophosphorous acid with hydroborate in acid solution gives only traces of phosphine whereas under similar conditions arsenic, antimony, germanium and tin oxyacids give good yields of their hydrides.[173]

Hypophosphorous acid is used as a colour stabilizer in the preparation of polymers, fatty materials and other organic products. It is used in plating without current,[134] particularly of nickel, although its salts are more often employed. It also has uses in the steel industry, the preparation of emulsifying agents and as a catalyst in the preparation of polyamides.[135–44, 191]

The addition of hypophosphites to radioactive waste solutions greatly reduces the volatility of ruthenium contained therein and thus prevents its escape when such solutions are concentrated for disposal.[174]

Hypophosphorous acid solution at 85°C. acts as a reducing agent for the disulphide linkage in cystine or oxidized glutathione, but does not reduce wool.[192] The crystalline acid reacts with orthocarbonates (orthocarboxylates) or ketals, yielding hypophosphite esters or 1-hydroxyalkyl phosphinates respectively.[193] A review of the chemistry and applications of hypophosphorous acid and its salts has appeared.[194]

## THE HYPOPHOSPHITES

The alkali metal hypophosphites are prepared by reaction of white phosphorus with an aqueous solution of alkali metal hydroxide usually with the addition of sufficient calcium hydroxide to remove the phosphite formed as calcium phosphite. They may also be prepared by double decomposition reactions with calcium hypophosphite, e.g. ammonium hypophosphite by reaction of the calcium salt with ammonium carbonate.[160] The reaction of phosphorus with hydroxides is strongly exothermic:

$$4P + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^-; \qquad \Delta F° = -80{\cdot}0\ \text{kcal.}^{123}$$

The technique of paper chromatography has been applied to the identification and determination of hypophosphites as for the other oxyacids of phosphorus.[73–4, 195] The solvents most often employed are those described by Volmar, Ebel and Yacoub.[73] The $R_f$ values of the hypophosphite anion in their acid and alkaline solvents are 0·84 and 0·75 respectively.[73–4] The chromatograms are normally developed by molybdate reagent. Hypophosphite itself does not give a colour with this reagent, but can be quantitatively oxidized to orthophosphate by acid sodium sulphite at 95°C.[196] Thin layer chromatography has also been used for the separation.[197–98]

The heats of solution of some of the hypophosphites have been determined and the values found are recorded in Table IV below.[71]

*Table IV.—Heats of Solution of Hypophosphites in Water*

| Salt | $-\Delta H$ in kcal./mole at $29 \pm 1$°C. | | |
|---|---|---|---|
| | Dilution in moles of water per mole of solute | | |
| | 100 | 1000 | ∞ |
| Ammonium hypophosphite | −2·20 | −1·66 | −1·60 |
| Sodium hypophosphite | +2·60 | +2·85 | +2·88 |
| Calcium hypophosphite | +1·70 | +3·90 | +4·20 |
| Barium hypophosphite | +0·20 | +0·68 | +1·05 |
| Barium hypophosphite monohydrate | −0·30 | −0·50 | −0·53 |

The alkali metal, alkaline earth and many other hypophosphites are soluble in water and the alkali metal salts are soluble in alcohol. The solubility of sodium hypophosphite over a range of temperatures is given below.

| Temperature °C. | 0° | 10° | 20° | 30° | 40° | 50° | 60° | 70° | 80° |
|---|---|---|---|---|---|---|---|---|---|
| Solubility in g. $NaH_2PO_2$ per 100 g. water | 104·7 | 107·5 | 112·3 | 120·3 | 131·0 | 145·1 | 163·9 | 188·2 | 220·5 |

Potassium hypophosphite has a solubility of 170·3 g. $KH_2PO_2$/100 g. water at 20°C. and 335 g./100 g. water at 100°C. Solubility data over a wider range of temperatures have been recorded for sodium and potassium hypophosphite, together with values of the density of solutions of various concentrations.[199] The figures for calcium hypophosphite are 15·3 g. $Ca(H_2PO_2)_2$/100 g. water at 25°C. and 12·5 g./100 g. at 100°C.[164] The solubilities at 20°C. of sodium and calcium hypophosphite in 100 g. of 98·2% and 86·5% aqueous glycerol have been given as 42·2 and 32·7 g. of sodium salt and 3·2 and 2·5 g. of calcium salt, respectively.[126]

Ammonium hypophosphite crystallizes as orthorhombic bipyramids and has a density of 1·634. There are four molecules to the unit cell which has the dimensions $a = 3{\cdot}98$ Å., $b = 7{\cdot}57$ Å. and $c = 11{\cdot}47$ Å. The space group is $Acmm(V_h^{21})$.[124] Ammonium hypophosphite decomposes when heated to 250°, giving ammonia and orthophosphoric acid in good yield. At higher temperatures the orthophosphoric acid loses water with the formation of polyphosphoric acid.[200]

Sodium hypophosphite, when heated, begins to decompose at about 310°C. giving, initially, phosphine, sodium phosphite, 'metaphosphate' and pyrophosphate. The bulk of the reaction proceeds according to the equations quoted below, although small amounts of phosphorus and phosphides of sodium are also formed.[76, 199, 201]

Water can be removed from the hydrate below 200° without decomposition occurring.[201]

At 310°C. $14NaH_2PO_2 \rightarrow 6PH_3 + 4Na_2HPO_3 + 2NaPO_3 + Na_4P_2O_7 + 3H_2O$
At 370°C. $4Na_2HPO_3 \rightarrow PH_3 + 2Na_3PO_4 + \frac{1}{2}Na_4P_2O_7 + \frac{1}{2}H_2O$
At 500°C. $NaPO_3 + Na_3PO_4 \rightarrow Na_4P_2O_7$

The reaction of hypophosphorous acid or hypophosphites with acetic anhydride has long been known to give a phosphorus suboxide, $(P_4OH)_n$,[175] but recently it has been found that potassium hypophosphite gives as a by-product a small amount of potassium acetophosphinate $K[HPO_2(COCH_3)]$.[176]

The sodium and lithium salts have also been prepared by neutralization of the acid (formed by ion exchange from the potassium salt).

The potassium salts of propionophosphinic and butyrophosphinic acid have been obtained similarly.

In aqueous solution hypophosphorous acid acts as a monobasic acid, the tautomeric tricovalent form being present only in trace amounts. However, a dipotassium compound has been prepared by causing a suspension of monopotassium hypophosphite to react in liquid ammonia with two equivalents of potassamide. The crystalline suspension is slowly converted to a white powdery solid which is extremely hygroscopic. On moistening the powder with a drop of water it decomposes with spontaneous combustion[146]:

$$KNH_2 + H_2PO.OK \rightarrow NH_3 + KHPO.OK$$

Although it is probable that the dipotassium compound contains a potassium–phosphorus bond, it is possibly a salt of the tautomeric form, viz. $HP(OK)_2$.

The hypophosphites of rubidium and cæsium are similar to those of the other alkali metals. The densities and solubilities of the salts increase with the atomic weight of the alkali metal. The cæsium salt crystallizes as a hemihydrate, $CsH_2PO_2,\frac{1}{2}H_2O$, with a density of 2·81 g./c.c. at 18°C. The rubidium salt is anhydrous and has a density of 2·32 g./c.c. at 17°C. Both salts are extremely deliquescent and have similar thermal decomposition reactions to those of the sodium salt.[95]

Like the acid, the alkali metal hypophosphites are powerful reducing agents. In fact, Latimer's figures[123] show hypophosphorous acid to be a much stronger reductant in basic solution than in acid solution. Again, many of the transition metal salts are reduced. Copper salts are reduced to the metal or the unstable hydride, unless chloride ions are present when cuprous chloride is formed.[77–9] Cobalt salts are similarly reduced but the product is more complex, being usually a mixture of the metal with metal phosphides.[80–1] Some workers, however, claim that unless ammonia is present a catalyst, such as palladium, is necessary for reaction to occur.[82] When palladium is present it is possible to obtain cobalt metal uncontaminated by phosphides. It is possible that, in this case, the reduction is effected by nascent hydrogen formed by the palladium-catalyzed aqueous oxidation of the hypophosphite. The volumetric determination of the hydrogen evolved from this catalytic dehydrogenation has been used for the estimation of sodium hypophosphite.[202]

The reduction of nickel salts is likewise dependent on the reaction conditions, the product being largely the metal, together with varying amounts of nickel phosphide. Palladium, again, can act as a catalyst and the presence of ammonia enhances the reaction rate besides decreasing the proportion of phosphide formed.[83–4] This reaction is utilized for the chemical deposition of nickel and there are many references of a technological nature.[85–7,96,130–4] It has been claimed that the mechanism represented by the equations:

$$H_2PO_2^- + H_2O \rightarrow HPO_3^{--} + 2H^+ + H^-$$
$$Ni^{++} + 2H^- \rightarrow Ni + H_2$$
$$H^+ + H^- \rightarrow H_2$$

is consistent with earlier data on the rate of hydrogen evolution during the reaction.[203] Other authors have invoked the reaction of hydroxyl radicals from the metal surface with partly dehydrogenated hypophosphite[204]:

$$H_2PO_2^- \rightarrow HPO_2^- + H$$
$$HPO_2^- + {\cdot}OH \rightarrow H_2PO_3^-$$
$$2H + Ni^{++} \rightarrow 2H^+ + Ni$$

Alloys of iron, nickel, chromium, cobalt and vanadium may be deposited on steel by reducing mixtures of salts of these metals with hypophosphites.[132, 162]

Although palladium and nickel salts are normally reduced to the metal (or a phosphide), if the metal is present in the form of a complex ion reduction may not be complete. Potassium tetracyanonickelate (II) and the corresponding palladate are both reduced to the monovalent cyanide by sodium hypophosphite in neutral or alkaline solution. The platinum analogue is not reduced.[88] Ruthenium, as halide or complex cyanide, is also reduced to the monovalent state but iridium and osmium salts show little or no change.[88]

Sodium hypophosphite can also reduce ferric iron to the ferrous state and this reaction has been employed for the colorimetric determination of iron by 2,2′-bipyridine or *o*-phenanthroline.[145]

Hypophosphite has been used as a precipitating agent for the gravimetric determination of scandium. The precipitate obtained consists of scandium trihypophosphite, $Sc(H_2PO_2)_3$,[177] $d$ 1·93, $n$ 1·56–1·58, sol. $3{\cdot}3 \times 10^{-4}$ M. at 25°.[209] The following transition metals are also said to give similar precipitates: Zr(IV), Hf(IV), Th(IV) and Ta(V).[177]

Sodium hypophosphite is also oxidized under conditions of glow-discharge electrolysis.[89] The reaction of iodine with solid anhydrous sodium hypophosphite at 50°C. is violently exothermic, and leads to inflammation. White, yellow or orange products of indeterminate composition are formed.[205] Nitrogen dioxide reacts with saturated alcoholic sodium hypophosphite solution at 20°C. giving a white precipitate. The water-soluble portion of this contains hypophosphite and phosphite, while the insoluble portion is assumed to be the sodium salt of the $(P^3)_6$ acid. Solid dinitrogen tetroxide at −10° oxidizes hypophosphite to phosphite, phosphate and condensed phosphates.[206]

Besides the uses already mentioned, the alkali metal hypophosphites are used in certain polymerizations[91–93] and the removal of oxygen from boiler water,[94] whilst the sodium, ammonium and the calcium salts have been used in the production of flameless, gas-producing charges.[128]

The alkaline earth hypophosphites are prepared similarly to the alkali metal salts. They are more soluble in water than the corresponding salts of most of the other oxyacids of phosphorus. These salts appear to have been little studied in recent years. Calcium hypophosphite has been reported to be phosphorescent after exposure to ultra-violet radiation.[97]

Aluminium hypophosphite may be prepared by reaction of aluminium hydroxide with hypophosphorous acid[98] or by heating an aluminium salt with 50% acid at 80–90°C. for 1 hr.[99] It can also be produced by double decomposition between sodium hypophosphite and an aluminium salt, but the precipitation is said to be slow. It is insoluble in water, sodium hypophosphite solution and hypophosphorous acid, but is dissolved by sodium hydroxide, hydrochloric acid and dilute sulphuric acid. The salt, as formed, is anhydrous and decomposes at 220°C. No double salts with aluminium chloride have been reported.[99]

Two gallium hypophosphites, the normal salt and an acid salt, have been reported.[100–1] The normal salt, which was claimed to have the formula $GaPO_2,H_2O$, was obtained as a white precipitate by adding sodium hypophosphite to a solution of gallium nitrate. It is insoluble in water, alcohol and ether, but is dissolved by dilute hydrochloric acid. The acid salt, given as $GaH_3(PO_2)_2$, is prepared by dissolving freshly precipitated gallium hydroxide in hypophosphorous acid. It is a white powder, soluble in warm water but insoluble in alcohol or ether.

Indium hypophosphite is obtained by double decomposition between a soluble indium salt and sodium hypophosphite. From the solution which remains after filtration of the precipitate, a basic indium hypophosphite is obtained by further concentration and addition of sodium hydroxide. This is a white, curdy precipitate corresponding to $In(H_2PO_2)_3,2In(OH)_3$. The normal salt is a white, crystalline powder readily soluble in mineral acids, but rather unstable to hydrolysis.[102]

Thallous hypophosphite is obtained as white, needle-like crystals by treating thallous carbonate with hypophosphorous acid and concentrating the solution. When heated for five days at 90–95°C. this compound gave a liquid, thought to be thallous phosphite.[103] The melting point of thallous hypophosphite has been reported to be 110°C.[103] although earlier workers gave 150°C.[98] The system thallous hypophosphite–water has a eutectic point at $-25$°C. with a composition of 13·5 mole-% of the salt.[104]

When a hydriodic acid solution of germanium dioxide is treated with a little hypophosphorous acid, a double hypophosphite-iodide, $3Ge(H_2PO_2)_2,GeI_2$, is obtained together with germanous phosphite and a phosphate, $Ge_3(PO_4)_2,2GeHPO_4$.[105] Double hypophosphite halides are also formed when germanium dioxide is heated with 50% hypophosphorous acid in the presence of hydrochloric or hydrobromic acid. The formulæ assigned to the two compounds are $Ge(H_2PO_2)_2,GeCl_2$ and $3Ge(H_2PO_2)_2,GeBr_2$.[106] The double hypophosphite-chloride and -bromide are fairly stable in air but are hydrolyzed to germanous hydroxide. Their respective melting points are 124° and 129°C. They are soluble in concentrated halogen acids and in phosphoric and hypophosphorous acids.[106] Reduction of germanium dioxide by hypophosphorous acid in 2–3% hydrochloric acid is said to give germanium or, possibly, a suboxide.[63] Other workers, however, found that germanium tetrachloride is reduced only to the divalent state by sodium hypophosphite under acid conditions.[148] There is also some evidence for the formation of germanic hypophosphite, $Ge(H_2PO_2)_4$, when germanous iodide is heated with 90% hypophosphorous acid in contact with the atmosphere, although this would appear to be at variance with other results.[105]

Stannous hypophosphite is prepared by cooling a solution of stannous hydroxide in hot 25% hypophosphorous acid. The hexahydrate, m.p. 66–67°C., which is formed is converted to the dihydrate by standing for 12 hr. at room temperature *in vacuo*. This melts at 70–90°C. and is converted to the anhydrous compound, m.p. 105°C., *in vacuo* at 45–50°C.[107]

When stannous hypophosphite in warm 25% hypophosphorous acid is treated with a little hydrochloric acid, the compound $3Sn(H_2PO_2)_2,SnCl_2$ (m.p. 130°C.) is obtained. Stannous chloride in 3N. hydrochloric acid gives a precipitate with hypophosphorous acid. This, dissolved in 50% hypophosphorous acid and made 10 N. with respect to hydrochloric acid, reacts with metallic tin to give crystals of the compound $Sn(H_2PO_2)_2,SnCl_2$ (m.p. 181°C.).[107] All these compounds of tin hydrolyze to stannous hydroxide and are decomposed by concentrated acids.

Stannic hydroxide is soluble in hypophosphorous acid but the solution does not yield any solid compound. The double salt, $Sn(H_2PO_2)_4,SnCl_4,3H_2O$, may be obtained by precipitation from a solution of stannic chloride with sodium hypophosphite[98] or by reaction of stannic chloride with 50% hypophosphorous acid in 3 N. hydrochloric acid solution.[107] It is insoluble in most solvents and is fairly readily hydrolyzed. It is decomposed by concentrated acids and, when heated, decomposes at 195°C. before melting. The anhydrous compound may be prepared by drying the hydrate *in vacuo* at 50–60°C. The corresponding iodide is obtained by the action of hypophosphorous acid on an alcoholic solution of stannic iodide. The solid darkens at 100°C., melts at 319°C., and decomposes above this temperature. It is insoluble in most solvents but dissolves in concentrated phosphorous acid, alkalis and hot hydrochloric acid solution. It is readily attacked by concentrated oxidizing acids.[108]

The hypophosphites of zinc and cadmium form loose addition compounds with

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hydrochloric and hydrobromic acids.[114] Although the addition is not completely stoicheiometric the compounds formed approximate to $Cd(H_2PO_2)_2,2HCl$; $Cd(H_2PO_2)_2,2\frac{1}{2}HBr$; $Zn(H_2PO_2)_2,HCl$ and $Zn(H_2PO_2)_2,HBr$.

A titanium hypophosphite has been prepared by causing a solution of titanium oxide in sulphuric acid to react with sodium hypophosphite. The amorphous white precipitate is easily hydrolyzed and is insoluble in most solvents. It may be dehydrated at 100°C. *in vacuo* over concentrated sulphuric acid. It is suggested that the two compounds are $H_2[Ti(OH)_4(H_2PO_2)_2]$ and $H_2[TiO_2(H_2PO_2)_2]$.[113] They are soluble in hot, concentrated acids and their aqueous suspensions have an acid reaction.

Recently thermometric titration of ferric chloride with sodium hypophosphite has provided evidence for complexes in which the iron:hypophosphite ratios are 1:1, 1:3 and 2:3.[118] Transport experiments by the same workers indicate that the 1:3 compound previously formulated[116, 117] as $[Fe_3(H_2PO_2)_6](H_2PO_2)_3$ should be regarded as being $Fe[Fe(H_2PO_2)_6]$ instead. However, the 1:1 complex of Cr(III) and hypophosphite has been shown to contain the $[CrH_2PO_2]^{2+}$ ion.[207]

Ferric, lead and copper hypophosphites have all been used in ammunition priming mixtures[109–12, 119–21] and sodium, calcium and ferric hypophosphites are much used in tonics.

Besides the scandium hypophosphite already mentioned[177, 208–9] the hypophosphites of other lanthanide and actinide elements have been described, including those of Th(IV), $UO_2$(II), Sm(III), Tm(III), Yb(III), La(III) and Y(III).[183,208] Their infra-red and Raman spectra are similar to those of hypophosphites of uni-and bivalent cations[183, 208] and their thermal decomposition appears to follow a similar course.[208–9]

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## SECTION XXII

# PHOSPHOROUS ACID AND THE PHOSPHITES

BY R. A. SMITH

## PHOSPHOROUS ACID

### Preparation

THE methods for the preparation of phosphorous acid described in Mellor, VIII, 900, remain in common use, although several innovations have been reported. The oxidation of phosphorus by water vapour under pressure[1] in the presence of 1·0–9·75 N. NaOH yields phosphoric, phosphorous and hypophosphorous acids, depending on the amount of sodium hydroxide present and the temperature. Use of the calculated quantity of sodium hydroxide results in the formation of disodium phosphite alone at temperatures below 225°C.; the phosphate is formed at temperatures above 250°C. With only the requisite quantity of sodium hydroxide to form the mono-sodium salt, a mixture of phosphite and hypophosphite is produced at temperatures below 225°C. It was also shown that sodium hypophosphite can be oxidized completely to phosphite or phosphate without the evolution of phosphine, by regulation of the amount of sodium hydroxide and the temperature.

The preparation of phosphorous acid of approximately 100% strength has been patented.[2] The preferred method is to mix phosphorus trichloride and 80–98% phosphorous acid at 86–90°C.; the product contains very little free water. Good yields have also been claimed to result from the hydrolysis of a mist of phosphorus trichloride droplets by steam at 150–200°C. in an inert atmosphere.[100]

A laboratory-scale preparation of this acid[3] has been described, based on the well-established reaction of phosphorus trichloride and water. This procedure has been claimed to give phosphorous acid of high purity, providing the phosphorus trichloride is freshly distilled and is hydrolyzed in an inert atmosphere with cooling.[101] An alternative method is to hydrolyze trialkyl phosphites under conditions such that any trialkyl phosphate is unaffected and may be removed by solvent extraction.[102] Phosphorous acid is also observed among the products of the electrochemical oxidation of white phosphorus at a porous anode,[103] or of the hydrolysis of the lower oxides of phosphorus,[104] though these are not suitable as preparative methods. The oxidation of phosphine by iodine in strong aqueous acid affords pure phosphorous acid in high yield.[134]

Attempts to prepare and isolate the two possible forms of phosphorous acid have occupied the attention of several workers. It was thought[4] that the presence of hydrochloric acid converted the $P(OH)_3$ form of phosphorous acid into the $HP:O(OH)_2$ form; therefore phosphorus trichloride was hydrolyzed in the presence of pyridine which would remove any hydrogen chloride formed. Despite this precaution no $P(OH)_3$ was obtained. Kolitowska[5] claimed that the highest yield of $P(OH)_3$ was obtained by hydrolysis of phosphorus tribromide and the lowest by hydrolysis of phosphorus trichloride. An optimum pH of 5·7, coupled with a low temperature during the hydrolysis, was said to favour a high yield of $P(OH)_3$.

A peroxy derivative[6] of phosphorous acid, having the formula $HP(:O)(OOH)(OH)$, is reported to be made by treatment of sodium hypophosphite solution with ozone.

**Refs. p. 641**

## METAL PHOSPHITES

### Preparation

The method of preparing alkali metal phosphites by addition of alkali to phosphorous acid was studied by Ebert,[7] who found it necessary to cause the acid to react with a solution of the appropriate alkali in ethanol to obtain a 98–99% yield, since the reaction in aqueous solution is hindered by the precipitation of phosphite.

The neutralization of phosphorous acid by sodium hydroxide dissolved in the minimum amount of water[2] gives, in addition to the already known sodium phosphites, two further compounds: $2NaH_2PO_3,H_3PO_3,\frac{1}{2}H_2O$, which dehydrates at 200°C., and $NaH_2PO_3,H_3PO_3$ which melts at 165°C. The existence of these compounds has also been confirmed by measurements of the specific electrical conductivity of the system $Na_2HPO_3$–$H_3PO_3$–$H_2O$.[105,106] Hydrolysis of phosphorus halides under alkaline, and mildly alkaline, conditions has been studied by Thilo and Heinz.[8] Chromatographic and iodometric analyses show that sodium phosphite is only one of a number of products. These authors obtained no evidence for the existence of $P(OH)_3$ and attributed the anomalous behaviour of the sodium bicarbonate hydrolysis to the formation of sodium pyrophosphite, $Na_2H_2P_2O_5$, the amount of which increases as more $PCl_3$ is added to the bicarbonate solution. A study of the $Li_2HPO_3$–$H_3PO_3$–$H_2O$ system at 25° disclosed three congruent phosphites, $LiH_2PO_3$, $LiH_2PO_3,H_3PO_3$ and $2LiH_2PO_3,H_3PO_3$, the last two compounds being white crystals, very soluble in water.[107]

The ternary system $K_2HPO_3$–$H_3PO_3$–$H_2O$[79] at 25°C. was studied by the solubility method. The phase diagram shows the existence of two acid phosphites with the formulæ $2KH_2PO_3,H_3PO_3$ and $KH_2PO_3,H_3PO_3$. These compounds have been isolated and their composition verified by *X*-ray and chemical analysis. A later study of the specific electrical conductivity of the system $K_2HPO_3$–$H_3PO_3$–$H_2O$ confirmed the existence of these compounds, and disclosed in addition the compound $KH_2PO_3,2H_3PO_3$. The formation of the more acid phosphites increases with rising concentration, temperature having a negligible effect. $KH_2PO_3,H_3PO_3$ is the most, and $KH_2PO_3,2H_3PO_3$ the least stable of the series.[108] A study of the rubidium and cæsium systems showed the presence of the series $MH_2PO_3,H_3PO_3$, $MH_2PO_3,2H_3PO_3$ (most stable), $2MH_2PO_3,H_3PO_3$ and $4MH_2PO_3,H_3PO_3$ (least stable): $(M = Rb, Cs)$. In each case the rubidium compound was more stable than the cæsium compound.[109]

In a study of the copper phosphites Nassler[80] characterized copper(II) phosphite dihydrate, $CuHPO_3,2H_2O$, copper(II) hydrogen phosphite, $Cu(H_2PO_3)_2$, copper(II) tetraminophosphite, $Cu(NH_3)_4HPO_3$, its dihydrate, and the di- and tri-hydrates of copper(II) pyridine phosphite, $CuHPO_3,2C_5H_5N,2$ or $3H_2O$. Pictorial representations of the *X*-ray powder photographs of these compounds are included in the paper. The thermal decompositions[81] of these compounds have been described and the results discussed in terms of loss of water, ammonia and pyridine.

Alkaline earth phosphites[9] are prepared by adding 82% of the calculated amount of carbonate or hydroxide to molten phosphorous acid at 80°C., stirring the mixture for several hours in ethanol or acetone in order to remove excess moisture and drying at 60°C. Good yields of pure products are reported. A similar method[13] is used to prepare ammonium phosphite which is also formed, together with mono- and diammonium phosphates, in the hydrolysis of $P_4N_6$.

Methods for preparing gallium[10–11] and thallium[12–13] phosphites have been described; there is some difference of opinion about the degree of hydration of $GaH_3(PO_3)_2$. Thallous phosphite is obtained on neutralizing phosphorous acid with aqueous thallous carbonate to the methyl-orange end point and evaporating the solution over phosphorus pentoxide *in vacuo*. The resultant oily product is dried by ethanol to give an amorphous, very hygroscopic solid, m.p. 30–50°C. A technique similar to that employed in the preparation of the alkaline earth phosphites is claimed to give a product of high purity. Normal thallium phosphite is a white crystalline substance which is stable in air up to 115°C.; its solubility at 20°C. is 23·80 g. per 100 g. of water. Acid phosphites, $TlH_2PO_3$ and $2TlH_2PO_3,H_3PO_3$, have been identified. Both are white compounds, congruently soluble in water. The compound $TlH_2PO_3,H_3PO_3$ was sought for, but could not be detected.[110]

Stannous phosphite[82] is prepared by adding tin(II) oxide to molten phosphorous acid. Water is added to the viscous solution; this results in the precipitation of transparent crystals which are washed with dry ethanol and dried in a vacuum.

A crystalline germanium phosphite,[14] $GeHPO_3$, has been observed as one of the products of the reduction of a solution of germanium dioxide in hydrochloric or hydrobromic acid with hypophosphorous acid.

Red-brown crystals of samarium phosphite[15] are prepared by metathesis of samarium chloride and a phosphite.

Rosenheim[16] drew attention to the similarity in crystal structure between complex phosphites and pyrophosphates, as for example in the complex dialkali uranium phosphites $R_2[UO_2(HPO_3)_2]$, which were similar to dialkali uranium pyrophosphates $R_2[UO_2(P_2O_7)]$; the analogy was, however, lacking with bivalent metal salts. A number of complex metal phosphites, including those of uranium, chromium, iron, cobalt and nickel, were prepared from solutions of the dialkali phosphite and the appropriate metal salt.

Addition[17] compounds are formed when hydrogen chloride is passed over dry phosphites; $CdHPO_3,2HCl$ and $PbHPO_3,2HCl$ have been prepared by this method.

A number of chromium phosphites have been reported. When phosphite ions[18] react in aqueous solution with $Cr^{++}$ cations, three types of compound are formed with Cr/P ratios of 1:1, 1:2 and 1:3. $CrHPO_3,H_2O$, $(NH_4)_2[Cr(HPO_3)_2],3H_2O$, $(NH_4)_2[Cr(HPO_3)_2]$ and $(NH_4)_4[Cr(HPO_3)_3],5H_2O$ have all been prepared and shown to be stable in air and slightly soluble in water. Chromic phosphite[19] is produced when sodium dichromate and phosphorous acid are mixed with a solution of alkali or ammonium sulphite at pH 6·2.

Triphosphitochromic acid[20, 83] may be prepared by dissolving chromium phosphite or chromium hydroxide in boiling aqueous phosphorous acid, followed by crystallization of the product. The proposed structure of the acid is shown in Fig. 1.

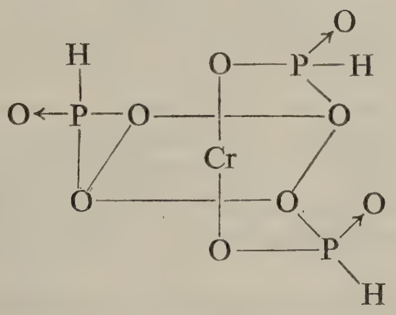


FIG. 1.—Proposed structure of triphosphitochromic acid

Its solubility in water and methanol at 15°C. is 11·70 g. per 100 g. and 3·82 g. per 100 g. solvent respectively. The density of the decahydrate at 20°C. is 2·03 g./c.c.; it is paramagnetic ($\chi = +7{\cdot}8 \times 10^{-3}$ at 20°C.) with a magnetic moment $\mu_{\text{eff}} = 3{\cdot}43$ which corresponds approximately to three unpaired electrons. The values of the pH after the addition of 0·5, 1·5 and 2·5 equivalents of alkali were used to calculate the dissociation constants:

$$pK_1 = 2{\cdot}65 \qquad K_1 = 3 \times 10^{-3}$$
$$pK_2 = 5{\cdot}42 \qquad K_2 = 4 \times 10^{-6}$$
$$pK_3 = 6{\cdot}44 \qquad K_3 = 4 \times 10^{-7}$$

The decahydrate was shown to lose ten molecules of water at 40°C. As the acid has a co-ordination number of six and three dibasic ligands it might be expected to be optically active. This has been confirmed by preparing the (+) tri-*d*-strychnine salt which has a molecular rotation of $[\alpha]^{M}_{Hg} = +420°$.

Aqueous ammonium triphosphitochromite shows optical density maxima at 435 and 590 mμ; this property has been used in estimating the instability constant which is $3{\cdot}4 \times 10^{-11}$. Ammonium and sodium triphosphitochromites are made by dissolving the bisphosphitochromites[16] in a solution of the alkali phosphites. Other triphosphitochromites can be prepared by metathesis from solutions of the sodium salt and the following cations: $Ba^{2+}$, $Cu^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Mg^{2+}$, $Zr^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Hg_2^{2+}$, $Al^{3+}$, $Ce^{3+}$, $Tl^{3+}$, $Sn^{2+}$, $Pb^{2+}$, $Cr^{3+}$, $UO_2^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$ and $Ni^{2+}$. The chromium salt is identical with chromium phosphite, $Cr_2(HPO_3)_3,7H_2O$.

A study of the system vanadium–phosphite[84] in water and acetic acid showed the existence of compounds with V:P mol. ratios of 2:3 and 1:2. These compounds have been isolated as $V_2(HPO_3)_3,7H_2O$ and $H[V(HPO_3)_2],3H_2O$.

The simple phosphite is prepared by mixing aqueous solutions of vanadium(III) perchlorate and ammonium phosphite, whilst the reaction of vanadium(III) acetate and phosphorous acid in 90% acetic acid produces the complex phosphite. Some properties of these compounds are tabulated below.

*Table I.—Properties of Vanadium Phosphites at* 20°*C.*

| Compound | Density g./c.c. | Magnetic moment $\mu_{eff}$B.M. | Solubility in water mol./l. |
|---|---|---|---|
| $V_2(HPO_3)_3,7H_2O$ | 1·89 | — | $<10^{-5}$ |
| $H[V(HPO_3)_2],3H_2O$ | 2·07 | 2·91 | $\sim10^{-3}$ |

The complex salt dissolved in excess phosphorous acid shows an absorption maximum at 685 mμ. A later study revealed the existence of complexes formed in solution with V:P mol. ratios of 1:1 and 1:2. The compound $VHPO_3,H_2O$ was isolated as pink-violet crystals insoluble in water or organic solvents, and slightly soluble in phosphorous acid or alkali metal phosphites. It was very sensitive to oxidation by traces of atmospheric oxygen.[111]

The reaction between anhydrous manganese(III) acetate[84] and a concentrated methanol solution of phosphorous acid produces a complex manganese salt, $H[Mn(HPO_3)_2],3H_2O$. Crystals of this compound have a density of 2·95 g./c.c. at 20°C. and a solubility in methanol of $10^{-4}$ mol./l. at 20°C. A solution of the compound in 0·5 molar methanolic phosphorous acid showed an absorption maximum at 500 mμ.

A series of iron phosphites has been prepared and examined.[85] The salts are mostly prepared from phosphorous acid and ferric nitrate phosphite, which in its turn is prepared from anhydrous ferric nitrate and phosphorous acid. The properties of the compounds prepared are given in Table II.

The existence of the complex ions $Fe(H_2PO_3)_n^{(3-n)+}$ ($n=1$ or 2) has been demonstrated. The stepwise instability constants of $Fe(H_2PO_3)_2^+$ (corrected to zero ionic strength) are $10^{-5}$ and $6{\cdot}7 \times 10^{-3}$ respectively.[112]

Nickel phosphite, $NiHPO_3,2H_2O$, and cobalt phosphite, $CoHPO_3,2H_2O$, have been described. They are sparingly soluble, and have an inverse temperature–solubility relationship (solubilities $5{\cdot}1 \times 10^{-3}$ and $2{\cdot}2 \times 10^{-3}$ mol./l. at 25°C., and $3{\cdot}0 \times 10^{-3}$ and $1{\cdot}6 \times 10^{-3}$ mol./l. at 85°C. respectively), probably due to the decomposition of complex ions.[113]

Complex platinum phosphites[21] are prepared by heating together potassium platinic chloride and phosphorous acid in a little water; compounds of the type

$Pt[P(OH)_3]_2[P(OH)_2O]_2$ and $Pt[P(OH)_3]_4Cl_2$ are produced after addition of alcohol.

### Reactions of Phosphites and Phosphorous Acid

The use of paper chromatography for the separation of phosphorus-containing anions[22-4] has assisted in identifying the products of the thermal decomposition of sodium phosphite.

*Table II.—Properties of Iron(III) Phosphites at 20°C.*

| Compound | Density g./c.c. | Magnetic moment $\mu_{eff}$,B.M. | Solubility mol./l. | |
|---|---|---|---|---|
| | | | Water | Methanol |
| $[FeHPO_3]NO_3$ | 1·99 | 5·89 | $7{\cdot}1\times10^{-5}$ | $2\times10^{-6}$ |
| $[FeHPO_3]Cl,6H_2O$ | 1·91 | — | $3{\cdot}0\times10^{-5}$ | $1\times10^{-6}$ |
| $Fe_2(HPO_3)_3$ | 2·40 | — | (a) | — |
| $Fe_2(HPO_3)_3,7H_2O$ | 2·27 | 5·83(b) | (a) | $5\times10^{-7}$ |
| $Fe_2(HPO_3)_3,9H_2O$ | 2·21 | — | (a) | — |
| $H[Fe(HPO_3)_2],3H_2O$ | 2·37 | 5·80 | (a) | $1{\cdot}17\times10^{-3}$ |
| $Fe(H_2PO_3)_3,H_2O$ | 2·38 | 5·81 | (a) | — |

[a] Hydrolyses.
[b] Calculated for one iron atom.

The dehydration of phosphorous acid or its salts does not lead to chain polyanions as considerable breaking or rearranging of the P–H bonds present in the phosphites occurs. There is no definite evidence to show the existence of anything more complex than pyrophosphite. Attempts to dehydrate beyond the pyrophosphite stage have resulted in the elimination of phosphine or hydrogen.

The results of a systematic examination[86] of the decomposition temperatures of various phosphites of the form $M^{I}_{2}HPO_3$ in air are given in Table III.

*Table III.—Decomposition Temperatures of Metal Phosphites in Air*

| | Temp. °C. |
|---|---|
| $Li_2HPO_3,2H_2O$ | 344 |
| $Na_2HPO_3,5H_2O$ | 292 |
| $K_2HPO_3,\frac{2}{3}H_2O$ | 250 |
| $Rb_2HPO_3$ | 350–400 |
| $Cs_2HPO_3,2{\cdot}5H_2O$ | 320 |
| $BeHPO_3,H_2O$ | ~400 |
| $MgHPO_3,5H_2O$ | 350 |
| $CaHPO_3,H_2O$ | 375 |
| $SrHPO_3,H_2O$ | 330 |
| $BaHPO_3$ | 475 |
| $ZrHPO_3,2H_2O$ | 255 |
| $CdHPO_3$ | 200 |
| $SnHPO_3$ | 320 |
| $PbHPO_3$ | 300 |
| $Tl_2HPO_3$ | 350 |

The products obtained after limited heating are never completely soluble in water, a result also noted by Ebel *et al.*[25] with disodium phosphite. Infra-red evidence shows that during heating the P–H bond disappears, but there is some evidence for the formation of the P–P bond.

Cæsium phosphite, $Cs_2HPO_3$, is the only phosphite for which the expected course of reaction, oxidation to phosphate followed by condensation to pyrophosphate, is largely followed. In the case of other phosphites radicals formed by the primary fission of P–H bonds rearrange or eliminate hydrogen or water. Certain hydrates eliminate water, passing through a series of intermediate hydrates before undergoing oxidative degradation.

The hydrogen phosphites,[86] of formula $M^{I}H(HPO_3)$ or $M^{II}H_2(HPO_3)_2$, give pyrophosphites on heating accompanied, or followed, by oxidative breakdown. The hydrated salts lose their water of crystallization before breakdown. Only lithium, sodium and strontium phosphites give well defined pyrophosphites. The temperatures at which the various hydrogen phosphites condense and then oxidize are given in Table IV.

*Table IV.—Decomposition Temperatures of Metal Hydrogen Phosphites in Air*

| | Temp. of condensation to pyrophosphite °C. | Temp. of breakdown °C. |
|---|---|---|
| $LiH_2PO_3$ | 205 | >300 |
| $NaH_2PO_3,2{\cdot}5H_2O$ | 158 | 330 |
| $KH_2PO_3$ | 180–200 | ~200 |
| $RbH_2PO_3$ | 220 | ~230 |
| $CsH_2PO_3$ | 280 | ~300 |
| $MgH_2(HPO_3)_2,3{\cdot}5H_2O$ | 230 | 250 |
| $CaH_2(HPO_3)_2,6H_2O$ | ~200 | 360 |
| $SrH_2(HPO_3)_2$ | 223 | 370 |
| $BaH_2(HPO_3)_2$ | 230 | ~250 |

A study of ammonium dihydrogen phosphite[87] shows that it decomposes to the pyrophosphite only when calcined barium oxide is present to remove the water liberated. Sodium acid phosphite, $NaH_3(HPO_3)_2$, if heated to 130°C. gives an acid pyrophosphite $NaH(H_2P_2O_5)$. Further heating to about 190° leads to a complex decomposition.

The transformations which take place when disodium phosphite is heated in the absence of oxygen have been described.[88] The author postulated an autoxidation–reduction above 400°C., $8P^{3+}H^{+} \rightarrow 4H_2 + P^{3-} + 7P^{5+}$. In the presence of alkali hydroxides this reaction is modified, since there is no autoreduction and up to 75% of phosphate is formed. The product on heating a mixture of monosodium phosphite and disodium phosphate dodecahydrate is $Na_3(HP_2O_6)$. The pyrolytic oxidation of phosphites has been investigated by Kolitowska.[26] When the disodium salt is heated in the range 300–400°C. in the presence of phosphoric acid[114] phosphine is evolved and acid sodium phosphate, which in turn condenses to polyphosphates, is formed. On boiling sodium phosphites with 85% aqueous sodium hydroxide, hydrogen is evolved[115–6] and orthophosphate is formed. Under milder alkaline conditions with trisodium phosphate,[117] sodium pyrophosphate is the product. In another study, a number of metal phosphites, $M_2(I)HPO_3$, $M(II)HPO_3$ and $M(I)H_2PO_3$, were heated at 200–475°. The normal phosphites decomposed to coloured products of uncertain composition in which the infra-red P–H stretching absorption had vanished, but which exhibited a reduced oxidation equivalent against acid Ce(IV), and hence might contain P–P bonded material. Acid phosphates dehydrated smoothly to pyrophosphites, but thereafter breakdown of the P–H structure occurred. Very acid salts such as $NaH_2PO_3,H_3PO_3$ also gave pyrophosphite, but then lost phosphorous acid by volatilization.[135] A mixture of disodium phosphite and iodine heated in a sealed tube at 180°C. gives acid sodium pyrophosphite and acid sodium hypophosphate, together with an unidentified phosphite. Analysis[27] of a solution of the product which is obtained by heating a mixture of disodium phosphite and a silver halide at 380°C. shows that it contains sodium trimetaphosphate, sodium triphosphate, metaphosphoric acid and the appropriate halogen acid.

Sodium phosphite reacts with sulphur[89] in an inert atmosphere to produce a mixture which contains monothiopyrophosphate. This may be separated by selective precipitation of the lead salt.

Sodium hypophosphate[90] is formed when sodium phosphite is made to react with lithium hydride at 330°C. under a nitrogen atmosphere.

A fluorine-substituted phosphorous acid[91] is produced by the interaction of phosphorous and hydrofluoric acids, $H_3PO_3 + 4HF \rightarrow HPF_4 + 3H_2O$. The total water content of the reaction mixture should not exceed 10% by weight.

Thermal decomposition of phosphorous acid in liquid medium[28] was shown to proceed via the following reactions: $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$ and $H_3PO_3 + H_2O \rightarrow H_3PO_4 + H_2$ in the temperature range 275–350°. Below 325°C. the composition of the evolved gases depends on the concentration of the solutions used and is independent of time. However when the duration exceeds fifteen hours at above 325°C. a secondary reaction sets in which decreases the proportion of phosphine. With concentrations below 50% of phosphorous acid nearly pure hydrogen is evolved, whilst above this concentration the phosphine content of the gases increases with increasing temperature. Bushmakin and Frost[29] confirmed these results and postulated that the reaction $PH_3 + 4H_2O \rightarrow H_3PO_4 + 4H_2$ takes place when the concentration of phosphorous acid is high.

More recent work on heating phosphorous acid[86] in a vacuum has shown that pyrophosphorous acid is initially formed. Decomposition in the presence of small partial pressures of water vapour leads to the formation of some phosphine, and red material comprising substantially phosphorus and pyrophosphoric acid. The proportions of these components are dependent on the temperature and time of heating. It was also noted[30] that the oxidation is catalyzed by the presence of colloidal platinum, silver and copper.

The reaction between phosphorous acid and iodine in aqueous solution has attracted the attention of a number of workers.[31–3] The work of Mitchell was reported in Mellor, VIII, 906. The system was re-investigated by Berthoud and Berger,[31] who found no need to postulate the existence of two forms of acid to account for the reaction. Nylén's investigations show that in weakly acid media (pH 3·2–6·8) the reaction is much faster than in strongly acid media and proceeds between $HPO_3^{--}$ and iodine. If iodine reacts with $H_2PO_3^-$ its specific rate is many times smaller than that with $HPO_3^{--}$. Iodine and $I_3^-$ react with $HPO_3^{--}$, the specific rate of the former being 1000 times that of the latter. Nylén also thought that the reaction is not subject to general acid catalysis, a view not supported by Griffith *et al.*,[34] who determined the catalytic coefficients of a few moderately strong acids. They concurred with the majority of Nylén's findings, but doubted whether the slow reaction between $HPO_3^{--}$ and $I_3^-$ could be detected. Similar reasoning to that of Nylén has been used by several authors to account for the mechanism of oxidation of phosphites with chlorine and bromine.

Blaser and Matei[35] showed that nitric acid free from oxides of nitrogen has no action on phosphorous acid. If, however, these oxides are present,[36] oxidation to phosphoric acid is rapid when the phosphorous acid concentration is greater than 44%. Other authors[37] consider this method to be unpractical for use on a commercial scale, because of the large quantities of nitric acid required.

The rate of oxidation of phosphorous acid by chromates[38] is more rapid in the presence of perchloric acid than in the presence of sulphuric acid or phosphoric acid.

The rate is much lower in acetate buffers, where $HCrO_4^-$ is the oxidizing species, and the reaction follows a complex rate law. The reaction is inhibited by chloride ion, which forms $CrO_3Cl^-$.[118] Oxidation of phosphite by permanganate, on the other hand, can be catalyzed either by 0·01% $OsO_4$, or by a 5% solution of Ni(II), Co(II), Cu(II) and $(NH_4)_2MoO_4$, an observation which has been applied to the analysis of phosphites.[101] Phosphite is also oxidized rapidly by persulphates. In neutral solutions the kinetics follow the rate law:

$$-\mathrm{d}(S_2O_8{}^{2-})/\mathrm{d}t = k_1+k_2[\textstyle\sum H_3PO_3]^{1/2}[S_2O_8{}^{-2}]^{3/2}$$

The oxidation is a chain reaction, propagated by the species $SO_4{}^-$, and initiated by the two parallel reactions:

$$S_2O_8{}^{2-} \rightarrow 2SO_4{}^-$$

and

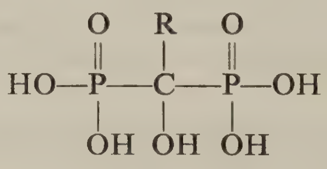
$$S_2O_8{}^{2-}+H_2PO_3{}^- \rightarrow SO_4{}^-+HSO_4{}^-+HPO_3{}^-(\text{ref.}^{119}).$$

The autoxidation of phosphorous acid[39] is induced by ozone and $O_2F$.

Several workers have reported on the anodic oxidation of phosphites. Lead anodes have been claimed as the most efficient, the sole detectable product being orthophosphate.[120] On a platinum anode the optimum conditions are 1–1·5 N. NaOH, 20°, c.d. 4–6 amp./dm.$^2$, when phosphite yields 30–40% orthophosphate, while hypophosphite is unaffected.[121] On palladium the rate-determining step of the oxidation is an initial catalytic dehydrogenation and not, as with hypophosphite, the ionization of the atomic hydrogen thus formed.[122]

Pyrophosphorous acid[40] is produced when phosphorus trichloride or tribromide reacts with phosphorous acid. The reaction $PX_3+5H_3PO_3 \leftrightarrows 3H_4P_2O_5+3HX$ is reversible and its rate appears to be governed by the solubility of the halogen acid in phosphorous acid.

The reaction of phosphorous acid[92–3] with organic acids, acid chlorides and anhydrides has been the subject of several patents. Compounds of the type



$$HO{-}\overset{O}{\overset{\|}{P}}(OH){-}\overset{R}{\overset{|}{C}}(OH){-}\overset{O}{\overset{\|}{P}}(OH){-}OH$$

are formed by refluxing the reactants. A simple equation cannot be written for the reaction which is very sensitive to temperature. Optimum yields are obtained if 1 g. mol. of acid reacts with 1·1 g. moles of acylating agent. The product from acetic anhydride is very soluble in water but may be recrystallized from glacial acetic acid. Anhydrous sodium formate, however, reacts with sodium phosphite at 370°C. according to the equation:

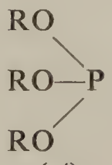
$$Na_2HPO_3+HCOONa \rightarrow H_2+CO+Na_3PO_4{}^{123}$$

Contrary to previous statements, good yields of alkyl iodides can be obtained by the action of alcohols and iodine upon phosphorous acid.[124]

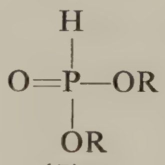
Dioxan and phosphorous acid[41] form a eutectic containing 52 mol.-% of acid with a freezing point of $-12$°C.; there is no evidence of interaction between the components.

## Structural and Physical Properties

The structure of phosphorous acid and the phosphites has attracted considerable interest because of the two possible alternatives:



and



$$O{=}\overset{H}{\overset{|}{P}}(OR){-}OR$$

(*A*) (*B*)

where R = hydrogen or an alkali metal.

*X*-Ray structure studies of crystalline phosphorous acid[42] and magnesium phosphite hexahydrate $MgHPO_3,6H_2O$ showed that the solids exist in form (*B*). Magnesium phosphite is isomorphous with magnesium sulphite hexahydrate $MgSO_3,6H_2O$ in which the positions of anions, cations and water molecules are probably very similar.

Further evidence for the structure of phosphorous acid and its salts is presented by Stelling[44] and Nylén.[45] The position of the absorption edge of the *K* line in the *X*-ray spectrum of phosphorus compounds has been found to depend on the number and type of the atoms connected directly to the phosphorus atom. The absorption edge for triply connected phosphorus atoms lies near 5·77 A. and for quadruply connected atoms near 5·75 A. According to evidence from this source it appears that phosphorous acid and its salts have a phosphorus atom connected to four neighbouring atoms.

The Raman spectra of phosphorous acid and its salts and esters[46–8] suggest a structure in the form of a distorted tetrahedron with the phosphorus atom connected to one hydrogen and three oxygen atoms. Tsuboi[49] obtained infra-red spectra of the phosphite ion both in the solid state and in solution. He assigned 980 and 1100 cm.$^{-1}$ as corresponding to $PO_3^{--}$ stretching vibrations and considered these to be characteristic of the $PO_3^{--}$ group. The nuclear magnetic resonance spectrum of phosphorous acid[50] also corresponds to one hydrogen atom being directly attached to the phosphorus atom in all phosphites except the triesters. The structural interpretations of the ultra-violet absorption spectra[51–4] of phosphites agree with the conclusions derived from other physico-chemical methods.

The literature on chemical evidence for the existence of one or the other form of phosphite has been reviewed by Nylén.[45] Arbuzov[55] used the formation of addition compounds with cuprous halides to demonstrate which of the phosphites has a triply connected phosphorus atom; the results agree with physico-chemical studies described above. Recent papers on this topic are by Voigt,[56] who attempted to prepare the form of phosphorous acid depicted as (*A*) in the diagram, and Kolitowska,[57] who stated that under identical conditions mild oxidants convert the 'enol' form of the acid to hypophosphoric acid and the 'keto' form to phosphoric acid.

Cryoscopic and molecular magnetic susceptibility studies of phosphorous acid dissolved in acetic acid suggest that in this solvent a dimeric form of $P(OH)_3$ is present, while in aqueous solution the $HPO(OH)_2$ form exists, also probably as a dimer.[125] The rate of exchange of $^{18}O$ between water and $H_3PO_3$ increases continuously with increasing acidity from pH 10 to 9·4 N. perchloric acid. Rate constants for exchange between water and various ionic species present were derived, but it was not possible to distinguish between several possible exchange mechanisms.[126]

The diameter of the $[H_2PO_3^-]$ ion in aqueous solutions of monosodium or potassium phosphite at 25° is 2·24 A.,[127] while that of the $[HPO_3^{--}]$ ion in solutions of the neutral salt is 2·66–3·04 A., the value decreasing with increasing dilution over the range 1 g. equiv./10–100 moles $H_2O$.[128]

Recalculation and new determinations of the ionization constants have led to a variety of results depending on the temperature and concentration of the solutions. Some of the results are given in Table V.

In highly acid solution phosphorous acid behaves as a very weak base ($[H_3PO_3][H^+]/[H_4PO_3^+] = 10^5$). The third dissociation constant, $[PO_3^{3-}][H^+]/[HPO_3^{2-}] = < 10^{-14}$. The same workers observed the following ionic mobilities: $l_{H_2PO_3^-} = 43{\cdot}4$; $l_{1/2HPO_3^{2-}} = 47{\cdot}8$; $l_{NaHPO_3^-} = 41{\cdot}5$; $l_{KHPO_3^-} = 39{\cdot}6$, while the instability constants of complexes at zero ionic strength are $KH_2PO_3$ 0·18; $NaH_2PO_3$ 0·11; $KHPO_3^-$ 0·16; $NaHPO_3^-$ 0·09.[129]

The protonation of phosphorous acid in aqueous sulphuric acid has been studied by proton magnetic resonance, though the p*Ka* values derived were not consistent with the scales of Hammett function derived for other types of base. Results could be interpreted in terms of a two-stage protonation:

$$H{-}O{-}H\cdots O{=}PH(OH)_2 \xrightarrow{H^+} H_2\overset{+}{O}{-}H\cdots O{=}PH(OH)_2 \rightarrow H_3\overset{+}{O} + H\overset{+}{P}(OH)_3 \text{ }^{136}$$

**Refs. p. 641**

In methanol, phosphorous acid behaves as a monobasic acid with a dissociation constant $k_1 = 3{\cdot}30 \times 10^{-5}$. The mobility of the dihydrophosphite ion in this medium, $l_{H_2PO_3^-} = 43{\cdot}0$.[130]

Using Kolthoff's data the free energies of formation of the ions have been calculated[59] to be: $H_2PO_3^-$ $-202{\cdot}35$ kcal. and $HPO_3^{--}$ $-194{\cdot}0$ kcal.

These values lead to the following potentials for the phosphorous–phosphoric acid couple:

$$H_2O + H_3PO_3 \rightleftharpoons H_3PO_4 + 2H^+ + 2e^- \qquad E^\circ = 0{\cdot}276 \text{ volts}$$
$$3OH^- + HPO_3^{--} \rightleftharpoons PO_4^{---} + 2H_2O + 2e^- \qquad E^\circ_\beta = 1{\cdot}12$$

The estimated entropies of $H_3PO_3$ and $H_2PO_3^-$ are 40 and 19 calories per degree respectively.

*Table V.—Ionization Constants of Phosphorous Acid*

| Temp. °C. | $K_1 \times 10^2$ | Solution concentration (molarity) | $K_2 \times 10^7$ | Solution concentration (molarity or ionic strength) | Reference |
|---|---|---|---|---|---|
| 0 | 0·97 | $5 \times 10^{-2}$ | 6·6 | $5 \times 10^{-2}$ ($\mu = 1$) | 32 |
| 17 | — | — | 82·5–179 | — | 94 |
| 18 | 1·6–6·2 | $10^{-3} - 10^{-1}$ | 2 | $\mu = 0$ | 95 |
| 18 | 1 | — | 2·6 | — | 96 |
| 20 | — | — | 8 | $\mu = 1{\cdot}15$ | 34 |
| 24 | — | — | 4·7 | — | 94 |
| 25 | 5 | — | 240 | — | 97 |
| 25 | 2–3 | $3 \times 10^{-2} - 10^{2}$ | 1·5 | $3 \times 10^{-2} - 10^{-2}$ | 58 |
| 30 | — | — | 5·9 | $\mu = 0{\cdot}4$ | 34 |
| — | ~6 | — | ~2 | $\mu = 0$ | 129 |

The conductivities of the system $Na_2HPO_3$–$H_3PO_3$–$H_2O$ have been measured[98] at 25, 35 and 45°C.

The heat of formation of sodium dihydrogen phosphite is $\Delta H^\circ_{298} = -338{\cdot}0$ kcal./mole[131] and of the disodium salt $\Delta H^\circ_{298} = -684{\cdot}2$ kcal./mole.[132] The heats of solution are as follows:

| | |
|---|---|
| $Na_2HPO_3,5H_2O$ | $\Delta H_{291} = +4{\cdot}54$ kcal./mole |
| $NaH_2PO_3$ | $\Delta H_{291} = -0{\cdot}90$ kcal./mole |
| $NaH_2PO_3,2{\cdot}5H_2O$ | $\Delta H_{291} = +5{\cdot}26$ kcal./mole |

All these heats of solution were determined at the concentration of one mole of crystals in 550 moles of water.

The solubility of disodium hypophosphite[133] in water at 25°C. has been found to be 38·4 g./100 g. solution. This determination was made in connection with an investigation of the system $Na_2HPO_3$–$NaH_2PO_2$–$H_2O$.

## Uses

Phosphorous acid and phosphites have been recommended as stabilizers for plastics. Incorporation of phosphites into several vinyl plastics[60–4] is claimed to stabilize them against heat and ultra-violet light; furthermore, it was found that washing these plastics with an acidified aqueous solution of phosphite removed iron impurities. In a review[65] of the action of polyvinyl chloride stabilizers it is suggested that evolution of HCl, with its catalytic action in degrading the polymer chain, forming carbonyl groups and conjugated double bonds, is followed by oxidation to the peroxide.

Experiments showed that when 2% of a basic lead phosphite is present in the polyvinyl chloride, evolution of hydrogen chloride, even on heating to 175°, is only slight and maximum retardation of opalescence occurs. Polyamides are also stabilized[66] by the addition of lead phosphite. Mixtures of lead phosphite[99] and boron compounds are also recommended as polyvinyl chloride stabilizers.

Lead phosphite has been used[67] in conjunction with sulphur, zinc oxide and accelerators when co-vulcanizing butyl rubber with a highly unsaturated rubber. The presence of the lead salt prevents blistering, porosity, inhomogeneity, delamination, cracking and peeling. The addition of up to 20% w/w of lead phosphite[68] to fluorine-containing elastomers increases the tensile strength but does not affect the percentage elongation. Phosphites are claimed[69] to be superior to other catalysts in condensing polyamides, 3% of phosphorous acid being optimal.

Corrosion by phosphorous acid vapours,[70] used to catalyze reactions such as the ethylation of benzene with ethane, can be prevented by passing the hot products over alkaline earth carbonate. The treatment of metal surfaces with phosphites to prevent rusting has been described in a number of patents. Kebrich[71] and Chiaudano[72] gave particulars of the use of basic lead phosphite as a pigment; details of the preparation of di- and mono-basic lead phosphites are given in Kebrich's patent. Treatment of the metal surface with mixtures containing phosphorous acid is claimed[73-5] to give good protection against rust formation and in one instance to improve lacquer adhesion of ferrous metal.[75] The addition of phosphites to boiler water[78] reduces the oxygen content and in doing so forms phosphates which are useful for the control of scale.

Various metals, including aluminium, copper, brass, cadmium and nickel, can be electro-polished anodically in a bath of 60–100% $H_3PO_3$ at 20–100°C. with an anodic current density of 5–100 amp./sq. dm.; to electro-polish zinc about 2% of hydrofluoric acid (40% w/w) must be added to 88% phosphorous acid.

A novel use of phosphorous acid[77] is its addition to fish water to prevent the formation of scale in the evaporator when the liquid is being boiled down.

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## SECTION XXIII

# HYPOPHOSPHORIC ACID AND THE HYPOPHOSPHATES

BY D. R. PECK

## THE PREPARATION OF HYPOPHOSPHORIC ACID

SEVERAL methods, which give better yields than the oxidation of white phosphorus previously reported (Mellor, VIII, 924), for preparing hypophosphoric acid and hypophosphates have been described.

In an early method[1] red phosphorus (5 g.) was oxidized by 10% bleaching powder solution (1 l), 64% oxidation being obtained. After filtering off the excess phosphorus, calcium hypophosphate and small amounts of calcium ortho-, pyro-, and metaphosphates were precipitated by neutralizing the filtrate with calcium carbonate. Treatment of the precipitate with dilute sulphuric acid gave a dilute solution of hypophosphoric acid.

The phosphorus recovered from the initial filtration was reddish-black in colour and was thought to be a new form of phosphorus. There is, however, very little evidence to support this[2] and the effect appears to be due to the particle size of the phosphorus. The smaller, light-red particles react more quickly with oxidizing agents, leaving behind the larger, darker particles.

A modification of the above procedure has been described[3] in which the oxidation is carried out at 25°C. The hypophosphate is first separated as the calcium salt, $Ca_2P_2O_6,2H_2O$. This is converted to the free acid by reaction with sulphuric acid and then to the tetrasodium salt, $Na_4P_2O_6,10H_2O$. Half the phosphorus is oxidized in the initial reaction and the yield is 16% based on the weight of phosphorus originally taken. This yield can be increased by 15% by oxidation of red phosphorus with an aqueous extract of bleaching powder at 12–15°, or better still, by the use of sodium chlorite containing a small proportion of hypochlorite, when $Na_4P_2O_6,10H_2O$ can be isolated.[100]

A similar reaction in which red phosphorus is stirred with sodium hypochlorite solution at 5°C. gives a 25% yield of disodium hypophosphate, $Na_2H_2P_2O_6,6H_2O$.[4] Oxidation of red phosphorus with iodine in solution at pH 4·6 to 5·7 gives a 34% yield of hypophosphoric acid.[5]

Strongly alkaline solutions of potassium permanganate or neutral alkaline solutions of hydrogen peroxide oxidize red phosphorus to orthophosphate and hypophosphate.

Yields of up to 40% of disodium hypophosphate, $Na_2H_2P_2O_6,6H_2O$, based on the phosphorus oxidized are obtained when sodium chlorite solution reacts with excess of red phosphorus. The equation given for the reaction is[6]:

$$2P + 2NaClO_2 + 8H_2O \rightarrow Na_2H_2P_2O_6,6H_2O + 2HCl$$

The reaction mixture is reported to contain 42% of hypophosphate, 35% of phosphite, 19% of orthophosphate and 2% of hypophosphite.[7] An apparatus in which the temperature of the reaction can be controlled has been described.[8] This gives slightly higher yields of sodium hypophosphate. The free acid was obtained by ion-exchange from solutions of the disodium ($Na_2H_2P_2O_6,6H_2O$) or the trisodium salt ($Na_3HP_2O_6, 9H_2O$), the latter being the more soluble in water.[8] The free acid may also be prepared by precipitating solutions of the sodium salts with lead acetate solution containing a little acetic acid. The resulting lead salt ($Pb_2P_2O_6$) is suspended in water and hydrogen sulphide is bubbled through the suspension for 7 hr. at 0°C. After removal of the lead sulphide, the filtrate is vacuum-evaporated at 10° to 20°C. under 3–7 mm. until the dihydrate of the acid crystallizes.[9,101]

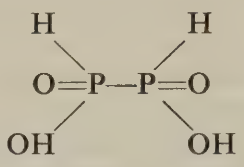
The reaction of an aqueous suspension of red phosphorus with sodium chlorite solution is strongly exothermic. If the temperature of the reaction mixture rises above 50°C., chlorine and chlorine dioxide are evolved and the yield of hypophosphate decreases. The reaction is catalyzed by hydrogen ions and there is usually an induction period on first mixing the reactants. During this period no apparent reaction takes place and the temperature rises but slightly. This may be followed by a sudden and almost explosive stage, particularly if more than 20% of the required amount of sodium chlorite has already been added to the phosphorus suspension. When more than 50 g. of phosphorus is taken initially, the reaction is best carried out by making a 15% wt.-vol. suspension of red phosphorus in 1% hydrochloric acid solution. This is cooled to 10–15°C. and a 25–30% wt.-vol. solution of sodium chlorite is slowly added with vigorous stirring of the reaction mixture, keeping the temperature below 30°C. The $NaClO_2/P$ weight ratio should be about 1·5. At the end of the reaction the excess phosphorus is filtered off, the filtrate is heated to 50° to 60°C. and is carefully adjusted to pH 5·0–5·5 by addition of pellets or a concentrated solution of sodium hydroxide. Any turbidity (due to the presence of iron and calcium) which forms is removed by filtration. On cooling the filtrate to room temperature, crystals of $Na_2H_2P_2O_6,6H_2O$ are quickly deposited. These should be purified from traces of other phosphorus compounds (mainly phosphite) by recrystallizing once or twice from water.

The preparation of hypophosphoric acid by the oxidation of red phosphorus with alkaline solutions of hydrogen peroxide, potassium permanganate, sodium hypobromite or sodium hypochlorite has been described. A similar oxidation occurs with acid solutions of sodium chlorate, sodium bromate or potassium persulphate. All these oxidations form phosphite, phosphate, pyrophosphate and polyphosphates as well as hypophosphate.[10] In addition the $P^5$–O–$P^4$–$P^4$ and $P^4$–$P^3$–$P^4$ anions are formed by the oxidation of red phosphorus by hydrogen peroxide in sodium carbonate solution, although from a medium made alkaline with sodium hydroxide a 23% yield of pure $Na_2H_2P_2O_6,6H_2O$ can be isolated.[102]

The oxidation of white phosphorus with dilute nitric acid in the presence of copper (Mellor, VIII, 925) gives yields of hypophosphoric acid accounting for not more than 15% of the phosphorus oxidized. This reaction has been shown to be violent if much phosphorus is used.[11] It is best carried out by adding the phosphorus in small pieces to a mixture of copper and dilute nitric acid heated to 100°C. It is reported that in addition to hypophosphoric acid the nitric acid oxidation forms acids of pentavalent and trivalent phosphorus, but no phosphorous acid. The oxidizing agent in the system is postulated to be copper nitrate, and this is partly reduced to copper and copper phosphides. The latter are then oxidized to oxy-acids of phosphorus by the excess copper nitrate.[12]

The hydrolysis of a number of phosphorus halides under mild oxidizing conditions yields hypophosphoric acid or its sodium salts in varying proportions with other tri- and penta-valent phosphorus compounds. A 45% yield of hypophosphoric acid is obtained by hydrolyzing diphosphorus tetraiodide and then oxidizing with iodine in solution at pH 5·7. Under similar conditions phosphorus tri-iodide gives a 37% yield of the acid.[13] Hydrolysis of diphosphorus tetraiodide at 0°C., followed by immediate oxidation with 30% hydrogen peroxide solution under alkaline conditions, converts 24% of the phosphorus to hypophosphate. If the oxidation is delayed for 24 hr. the yield falls to 10%. The initial product of the hydrolysis appears to be $P_2(OH)_4$ and this on oxidation yields hypophosphoric acid. The final products include hydrogen iodide, $P_{12}H_6$, phosphine, hypophosphorous, phosphorous and phosphoric acids.[14]

More recent work confirms that the initial product in the hydrolysis of diphosphorus tetraiodide is the acid $P_2(OH)_4$ or $H_4P_2O_4$. The structure of this is as follows:



and it is more stable at pH 7 than in acid or alkaline solution. Oxidation by atmospheric oxygen, or by iodine in acid or alkaline solution readily converts it to hypophosphoric and pyrophosphoric acids.[15] On the basis of the newer nomenclature for the reduced acids of phosphorus, $H_4P_2O_4$ is referred to as $\overset{2}{P}$–$\overset{2}{P}$ acid[16] (see also page 596).

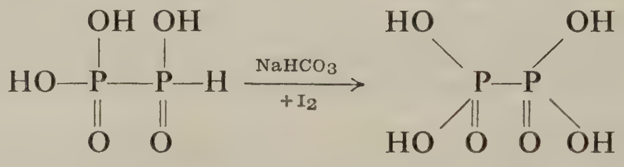
At 20°C. solutions of diphosphorus tetraiodide in carbon disulphide readily absorb oxygen to give phosphorus tri-iodide and the polymeric compound $(P_3I_2O_6)_n$. The reaction may be written:

$$7P_2I_4+6O_2 = 8PI_3+\frac{2}{n}(P_3I_2O_6)_n$$

Hydrolysis of the polymer gives some hypophosphoric acid, together with phosphine and phosphorous and phosphoric acids.[17]

A 55% yield of hypophosphoric acid is obtained by slowly adding phosphorus tribromide to an ice-cold solution of sodium acetate and acetic acid at pH 5·7. The product is then oxidized in the presence of sodium bicarbonate with sufficient 0·10 N. iodine solution to convert 60% of the trivalent phosphorus to the pentavalent form. Orthophosphate and hypophosphate are then precipitated by adding barium nitrate. Hypophosphate is recovered as the silver salt by dissolving the precipitate in dilute phosphoric acid and adding silver nitrate.[18] A similar reaction using phosphorus trichloride gives a 10% yield of hypophosphoric acid.[19]

The mechanism of the hydrolysis of the phosphorus trihalides has been explained in terms of the two isomers of phosphorous acid. The less stable form, $P(OH)_3$,[20] is said to give hypophosphoric acid, whereas the more stable form, $HO.P(OH)_2$, gives phosphoric acid.[21] Phosphorus tribromide is reported[21] to give more of the unstable isomer on hydrolysis. The opposite view, i.e. that hypophosphoric acid is formed by oxidation of the $HO.P(OH)_2$ isomer, has also been used[19] to explain the mechanism. However, it is more likely that the reaction involves the intermediate formation of a lower oxyacid of phosphorus. For example, diphosphorous acid has been isolated from the hydrolysis products of phosphorus tribromide.[22] This acid is readily oxidized by iodine in sodium bicarbonate solution to form hypophosphoric acid:



When phosphorus trichloride vapour is passed into sodium bicarbonate solution at 0°C. the disodium salts of phosphorous and pyrophosphorous acids are formed, together with phosphine and other oxyacids in smaller amounts. The initial product is disodium phosphite and this reacts with more phosphorus trichloride to give disodium pyrophosphite:

$$Na_2HPO_3+PCl_3+2H_2O \rightarrow Na_2H_2P_2O_5+3HCl$$

Smaller amounts of pyrophosphite and larger quantities of the other products are formed by hydrolyzing the trichloride under more alkaline conditions. When the hydrolysis products are oxidized with iodine in sodium bicarbonate solution, the pyrophosphite is oxidized extremely slowly, whereas the diphosphite rapidly forms hypophosphate. The latter is stable under these conditions of oxidation.

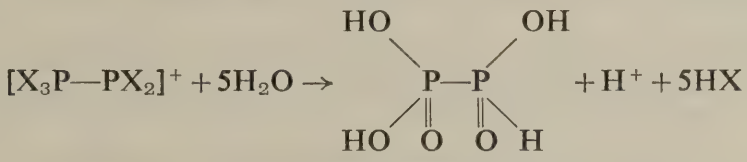
Liquid phosphorus tribromide and sodium carbonate solution at 0°C. react to give much larger quantities of diphosphite, but no pyrophosphite is formed. A similar reaction between sodium bicarbonate solution and phosphorus tri-iodide dissolved in carbon disulphide gives a smaller proportion of diphosphite than in the products obtained from phosphorus tribromide. Again no pyrophosphite is formed.

No evidence was found to indicate the presence of an unstable form of phosphorous acid, $P(OH)_3$, in these reactions. It seems reasonably certain therefore that hypophosphoric acid results from the formation and subsequent oxidation of diphosphorous acid. The experimental observations suggest that P–P bonds are more easily formed as the phosphorus–halogen bond (P–X) becomes less polar. The mechanism can be interpreted in terms of a proton transfer reaction as follows:

$$PX_3 + H^+ \rightarrow [HPX_3]^+ \rightarrow [PX_2]^+ + HX$$

The $PX_2{}^+$ radical then reacts with a further halide molecule to form an intermediate compound which is hydrolyzed by water to form diphosphorous acid.[23]

$$[PX_2]^+ + PX_3 \rightarrow [X_3P—PX_2]^+$$



$$[X_3P—PX_2]^+ + 5H_2O \rightarrow (HO)_2P(O)—P(O)(OH)H + H^+ + 5HX$$

Hypophosphoric acid is also formed by oxidizing diphosphorous acid with iodine in 0·01 N. hydrochloric acid solution, but the oxidation proceeds more slowly than in weakly alkaline solution. Increasing the acidity decreases the yield of hypophosphate and, with concentrations above normal, increasing hydrolysis of the product occurs. The oxidation also decreases in strongly alkaline solutions.

Hypophosphoric and phosphorous acids are formed when diphosphorous acid is decomposed by heating with sodium hydroxide alone:

$$H_4P_2O_5 + H_2O \rightarrow 2H_3PO_3$$
$$H_4P_2O_5 + H_2O \rightarrow H_4P_2O_6 + H_2$$

No phosphine is formed in these reactions and the proportions of the two acids produced are influenced by the sodium hydroxide concentration as shown in Table I.[24]

*Table I.—The Decomposition of Diphosphorous Acid with Concentrated Sodium Hydroxide Solutions*[24]

| Time (hr.) | Temp. °C. | NaOH % | % P as $H_3PO_3$ | % P as $H_4P_2O_6$ |
|---|---|---|---|---|
| 6 | 118 | 30 | 29·7 | 26 |
| 3 | 130 | 40 | 33 | 59·6 |
| 6 | 130 | 40 | 36 | 60 |
| 12 | 130 | 40 | 35·6 | 61 |
| 1 | 160 | 60 | 14·5 | 81 |
| 1 | 160 | 60 | 19·2 | 81 |
| 0·3 | 180–190 | 80 | 11·5 | 84 |

Finely powdered disodium phosphite and excess of lithium hydride when heated at 330°C. in a nitrogen atmosphere form a mixture of phosphorus compounds and lithium nitride. About 30% of the phosphite is converted to hypophosphate. The reactions are given as:

$$
\begin{gathered}
2Na_2HPO_3+2LiH \rightarrow NaPO_2+Na_3PO_4+2Li+2H_2 \\
Na_2HPO_3+7LiH \rightarrow Li_3P+2Li_2O+Na_2O+4H_2 \\
6Li+N_2 \rightarrow 2Li_3N \\
2Na_2HPO_3+2LiH \rightarrow Na_4P_2O_6+2Li+2H_2
\end{gathered}
$$

The last of the above reactions is supposed to proceed by the formation of the free radical $Na_2PO_3\cdot$:

$$Na_2HPO_3+LiH = Na_2PO_3\cdot+Li+H_2$$

This radical can then dimerize to form hypophosphate or disproportionate to orthophosphate or to metaphosphite ($NaPO_2$).[25]

Hydrolysis of diphosphorus tetraiodide, or of the phosphorus sulphides $P_4S_3$, $P_4S_5$ and $P_4S_7$, with hydrogen peroxide in solutions of sodium bicarbonate, carbonate or hydroxide gives 15–30% yields of hypophosphate. The major product is phosphate (30–60%) and minor amounts of phosphite and the $\overset{4}{P}–\overset{3}{P}–\overset{4}{P}$ and $\overset{5}{P}–O–\overset{4}{P}–\overset{4}{P}$ acids are also formed. The reaction with phosphorus pentasulphide is given as[26]:

$$P_4S_7+30H_2O_2+22NaOH \rightarrow Na_4P_2O_6+2Na_2HPO_4+7Na_2SO_4+40H_2O$$

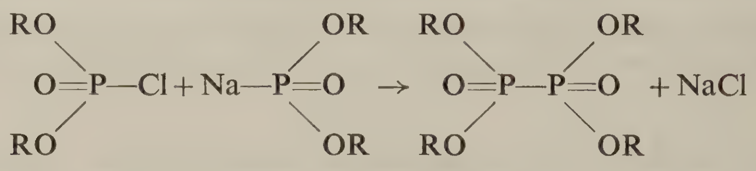
It is reported that at 300°C. a mixture of disodium phosphate and ammonium nitrate gives a product having the formula $Na_4P_2O_6,4H_2O$. Similarly, potassium nitrate and monopotassium phosphate are said to give $K_4P_2O_6,4H_2O$.[27] There is, however, little evidence that these are hypophosphates and the compounds would seem to be either poly- or meta-phosphates.

No exchange of radioactive phosphorus between phosphorous and phosphoric acids according to the mechanism:

$$H_3{}^{32}PO_4+H_3PO_3 \rightleftharpoons H_4{}^{32}PPO_6 \rightleftharpoons H_3PO_4+H_3{}^{32}PO_3$$

was found in acid or alkaline solution. In 5·6 N. HCl the equilibrium constant for the formation of hypophosphoric acid from phosphorous and phosphoric acids is less than $8\times10^{-5}$ l. mole$^{-1}$ at 25°C.[28]

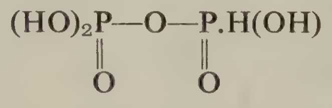
Esters of hypophosphoric acid have been obtained by reaction of the sodium salts of esters of phosphorous acid with phosphorochloridites according to the equation[29]:



The menthyl ester obtained in this way dissociates into menthene and hypophosphoric acid.[30] A general method for preparing tetra-alkyl hypophosphates in 40–70% yield is to cause dialkyl sodium phosphites to react with sulphuryl chloride at 5° to 10°C. according to the equation[31]:

$$2(RO)_2NaPO+SO_2Cl_2 \rightarrow (RO)_2OP.PO(OR)_2+2NaCl+SO_2$$

Isohypophosphoric acid, the isomeric form



$$(HO)_2\underset{\displaystyle O}{\underset{\|}{P}}—O—\underset{\displaystyle O}{\underset{\|}{P}}.H(OH)$$

of the acid has been obtained in 27% yield by neutron bombardment of disodium orthophosphate at low temperature. Smaller amounts of ordinary hypophosphate, pyro- and tripoly-phosphate and some unknown species are also formed.[32]

Isohypophosphates have also been obtained by dehydrating mixtures of phosphoric and phosphorous acids under reduced pressure or by heating mixtures of mono- and di-sodium phosphites at 180°C. *in vacuo*. Trisodium hypophosphate is the main product of the reaction between phosphorus trichloride and phosphorous and phosphoric acids in the absence of added water at 50°C. The reaction mixture is then neutralized with sodium bicarbonate and crystallized[23]:

$$PCl_3 + 3H_3PO_4 + 2H_3PO_3 \rightarrow 3H_3(HP_2O_6) + 3HCl$$

Oxidative hydrolysis of phosphorus tribromide gives some isohypophosphate, but apparently in lower yield than the trichloride reaction with phosphorous and phosphoric acids.[22] However, when both halides are oxidized and hydrolyzed under alkaline conditions, the bromide gives the better yield.[23]

At 150° to 160°C. in the presence of silica gel as catalyst 1 mol. of bromine reacts with 2 mol. of disodium phosphite to give isohypophosphate as the primary product:

$$2Na_2HPO_3 + Br_2 \rightarrow Na_3HP_2O_6 + NaBr + HBr$$

However, further reaction occurs to give phosphite, pyrophosphite, ortho-, meta-, pyro- and poly-phosphates and phosphorus hydrides. As a result the final yield of isohypophosphate is only about 5%.[33]

Several reactions are known in which isohypophosphates are formed by exchange processes between phosphorous acids of different complexity. For example, neutral aqueous solutions containing equimolar proportions of sodium pyrophosphite and disodium phosphite react slowly at room temperature according to the equation[34]:

$$Na_2HPO_3 + Na_2H_2P_2O_5 \rightarrow Na_3HP_2O_6 + NaH_2PO_2$$

These are mentioned under the properties of hypophosphoric acid and are discussed in more detail in Section XX (page 604). As methods of preparation the more suitable reactions are as follows.

A 12% yield of the sodium salt, $Na_3HP_2O_6,8H_2O$, is obtained by adding 3 mol. of phosphorus trichloride to a mixture of 1 mol. of monosodium phosphate and 2 mol. of disodium phosphate dissolved in 1900 ml. of water, in the presence of 1400 g. of sodium bicarbonate at 0°C. A somewhat better yield results when dipotassium phosphate and potassium bicarbonate are used. Phosphorus oxychloride reacts at 0°C. with a 40% wt.-vol. solution of phosphorous acid in the presence of excess of sodium bicarbonate to give a yield of about 20% of isohypophosphate.[35] Very high yields are obtained by heating together concentrated aqueous solutions of orthophosphates and pyrophosphites. 95 g. of $Na_2H_2P_2O_5$ are added to 537 g. of $Na_2HPO_4,12H_2O$ dissolved in 100 ml. of water at 100°C. The mixture is heated for 3 min., 300 ml. of water are added and the mixture quickly cooled and filtered. The filtrate is treated with iodine in sodium bicarbonate solution to oxidize unwanted reduced acids and the isohypophosphate is purified by conversion with lead acetate to the lead salt and subsequent decomposition with sodium sulphide. The yield is 112 g. (58%) of $Na_3HP_2O_6,8H_2O$. If the reaction is carried out at 30°C. the yield is 75% and this can be increased to 96% by using 6 molar dipotassium phosphate solution. The optimum acidity is pH 5–8 and yields decrease as the temperature is raised or the orthophosphate concentration is lowered.[36] The pyrophosphite may be prepared by neutralizing phosphorous acid with one equivalent of sodium hydroxide. The crystalline product ($NaH_2PO_3,2\frac{1}{2}H_2O$) is then dried *in vacuo* at 60°C. and the anhydrous salt is further heated *in vacuo* at 150°C.[37–8]

$$2NaH_2PO_3 \rightarrow Na_2H_2P_2O_5 + H_2O$$

Suitable methods of preparation for hypophosphoric acid and its mono-, di-, tri- and tetra-sodium salts have been given.[101]

The mechanism of the formation of hypophosphates has been reviewed.[39]

## THE PREPARATION OF SALTS OF HYPOPHOSPHORIC ACID

Many of the known salts of hypophosphoric acid were prepared during the last century, following the discovery of the acid in 1792 by Pelletier.[40] Detailed information on the methods of preparation of the earlier known salts is to be found in the work of Salzer,[41] and this has already been summarized (Mellor, VIII, 931–40). Later work has substantially confirmed the previous findings and has extended the number of salts. Table II lists the salts which have already been described. Those which have since been reported are discussed below.

Magnesium hypophosphate, $Mg_2P_2O_6,12H_2O$, is reported to be converted to the di-, tri- and hexa-hydrates on crystallizing from acetic acid containing a little hydrochloric acid.[42] The optical properties and crystal morphology of the dodecahydrate are stated to be almost identical with those of a substance formulated as $Mg_2H_2P_2O_7,11H_2O$.[43] A silver salt, $Ag_4H_2P_2O_7$, is said to exist. Addition of magnesium powder to a solution of disodium hypophosphate is reported to form, in acetic acid solution, a product having the apparent composition $Mg_2P_2O_6,Mg_2H_2P_2O_7,13H_2O$ from which the salt $Ag_4P_2O_6,Ag_4H_2P_2O_7$ is derived.[44]

Lead hypophosphate, $Pb_2P_2O_6$, and acid barium hypophosphate, $BaH_2P_2O_6,2H_2O$, have been prepared in the pure state by reaction of disodium hypophosphate solutions with lead acetate and with barium chloride in the presence of hydrochloric acid. An aqueous suspension of the barium salt reacts with ammonium sulphate solution to form diammonium hypophosphate. A solution of this forms the monoammonium salt on stirring with a 48% solution of the free acid and then evaporating *in vacuo* over phosphorus pentoxide.[9]

*Table II.—The Salts of Hypophosphoric Acid*

$Li_2H_2P_2O_6,2H_2O$
$Li_4P_2O_6,7H_2O$
$NH_4H_3P_2O_6$
$(NH_4)_2H_2P_2O_6$
$(NH_4)_4P_2O_6$
$NH_4.N_2H_5.H_2P_2O_6$
$N_2H_5.H_3P_2O_6$
$(N_2H_5)_2H_2P_2O_6$
$(NH_3OH)_2H_2P_2O_6$
$(CN_3H_6)_4P_2O_6,2H_2O$*
$NaH_3P_2O_6,2H_2O$
$Na_3H_5(P_2O_6)_2$
$Na_2H_2P_2O_6,6H_2O$
$Na_5H_3(P_2O_6)_2,20H_2O$
$Na_3HP_2O_6,9H_2O$
$Na_4P_2O_6,10H_2O$
$Na_4P_2O_6,2MoO_3$
$Na_4P_2O_6,4MoO_3,16H_2O$
$Na_2K_2P_2O_6,9H_2O$
$NaCo(NH_3)_6P_2O_6,3H_2O$
$Na_2CoP_2O_6,1\frac{1}{2}H_2O$
$Na_4Ni_2(P_2O_6)_2,24H_2O$
$KH_3P_2O_6$
$K_2H_2P_2O_6,2H_2O$
$K_2H_2P_2O_6,3H_2O$
$K_3H_5(P_2O_6)_2,2H_2O$
$K_3HP_2O_6,3H_2O$
$K_4P_2O_6,2H_2O$
$K_4P_2O_6,8H_2O$
$K_6CuH_8(P_2O_6)_4,15H_2O$
$3K_2H_2P_2O_6,ZnH_2P_2O_6,15H_2O$
$K_2H_2P_2O_6,CdH_2P_2O_6,2\frac{1}{2}H_2O$
$K_2CoP_2O_6,5H_2O$
$3K_2H_2P_2O_6,NiH_2P_2O_6,15H_2O$
$K_2H_2P_2O_6,MnH_2P_2O_6,3H_2O$
$3K_2H_2P_2O_6,CoH_2P_2O_6,15H_2O$
$K_2NiP_2O_6,6H_2O$
$Rb_2H_2P_2O_6,2H_2O$
$Rb_4P_2O_6,10H_2O$
$Ag_4P_2O_6$
$Hg_2P_2O_6$
$Cu_2P_2O_6,6H_2O$
$Cu_2P_2O_6,H_2O$
$CaH_2P_2O_6,6H_2O$
$Ca_2P_2O_6,2H_2O$
$SrH_2P_2O_6,3H_2O$
$Sr_2P_2O_6,2H_2O$
$BaH_2P_2O_6,2H_2O$
$Ba_2P_2O_6,2H_2O$
$Be_2P_2O_6,3H_2O$
$MgH_2P_2O_6,4H_2O$
$Mg_2P_2O_6,12H_2O$
$Zn_2P_2O_6,2H_2O$
$Cd_2P_2O_6,2H_2O$
$Tl_2H_2P_2O_6$
$Tl_3HP_2O_6$
$Tl_4P_2O_6$
$Mn_2P_2O_6$
$Co_2P_2O_6,8H_2O$
$Ni_2P_2O_6,12H_2O$
$Pb_2P_2O_6$
$ThP_2O_6,11H_2O$
$ZrP_2O_6,H_2O$

* Guanidine salt.

The silver, mercurous, copper, lead, cobalt and nickel salts have all been made by mixing equimolar proportions of solutions of the metal acetate and disodium hypophosphate. All the salts decompose on heating to give the metal. The decomposition of the mercurous salt is explosive. In a nitrogen atmosphere at temperatures below 200°C. the silver, mercury and copper salts give the following products[45]:

$$Ag_4P_2O_6 \rightarrow Ag + (PO_3)_3 + (PO_3)_n$$
$$Hg_2P_2O_6 \rightarrow Hg + (PO_3)_3 + (PO_3)_n + PO_4 + P_2O_7 + P_3O_{10}$$
$$Cu_2P_2O_6 \rightarrow Cu + PO_4 + P_2O_7 + P_3O_{10} + P_4O_{13} + P_5O_{16}$$

Ceric hypophosphate, $CeP_2O_6,xH_2O$, has been obtained as a yellow gel by reaction of a solution of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, in N. nitric acid with a solution of sodium hypophosphate.[3] The substance is stable at 100°C. but at 150°C. it becomes colourless, owing to the decomposition:

$$6CeP_2O_6 \rightarrow 2Ce(PO_3)_3 + Ce_4(P_2O_6)_3$$

Thorium hypophosphate, $ThP_2O_6,2H_2O$, is formed by controlled precipitation of a hot thorium nitrate solution with a solution of disodium hypophosphate.[46] The neodymium salt, $Nd_4(P_2O_6)_3$, and the yttrium salt, $Y_4(P_2O_6)_3$, have been obtained in a similar manner.[47] Protoactinium salts give a precipitate with tetrasodium hypophosphate. The product is also insoluble in 5 N. sulphuric acid.[48]

A sesqui-hydrated tetrasodium hypophosphate, $Na_4P_2O_6,1\frac{1}{2}H_2O$, has been reported and the transition temperature between this and the decahydrate is given as 74·6°C. Anhydrous tetrasodium hypophosphate is stable to heat above 400°C., but the acid salts decompose at lower temperatures, giving a mixture of condensed phosphates and a trace of a brown product of high phosphorus content.[101] The sodium ammonium salt, $Na_2(NH_4)_2P_2O_6,7H_2O$, has been made. Copper and nickel form the complex salts $NH_4CuP_2O_6,4H_2O$ and $Na_2NiP_2O_6,12H_2O$. Electrolysis of solutions of these two salts shows that the heavy metal atom is in the anion.[49]

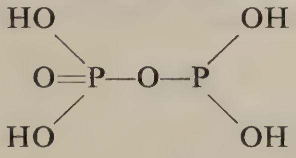
Tripotassium isohypophosphate has been prepared from dipotassium orthophosphate and phosphorus trichloride[35] in a manner similar to the trisodium salt (see p. 604):

$$K_2HPO_4 + 4KHCO_3 + PCl_3 \rightarrow K_3HP_2O_6 + 3KCl + 2H_2O + 4CO_2$$

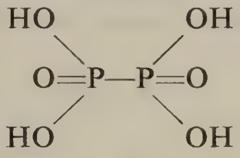
## THE STRUCTURE OF HYPOPHOSPHORIC AND ISOHYPOPHOSPHORIC ACID

With the information which was available in the earlier literature it was not possible to give a precise structure or formula for hypophosphoric acid. The evidence used to support the various structures which were proposed has previously been given in some detail (Mellor, VIII, 926–8). Many of the facts and observations known at that time were apparently contradictory and the formula of hypophosphoric acid was confused with those of other lower acids of phosphorus. In the light of present and more certain knowledge, the main features of the earlier work are as follows.

Before 1933, argument was largely concerned with the question as to whether the molecular formula of the acid was $H_2PO_3$ or the double one $H_4P_2O_6$. Salzer[41] had originally adopted the double formula on the basis of being able to prepare four different salts with monovalent cations. He concluded that the structure was represented by I or II, of which he favoured the first.



I

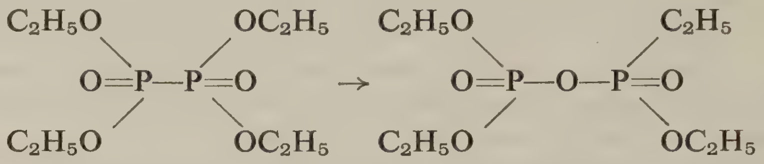


II

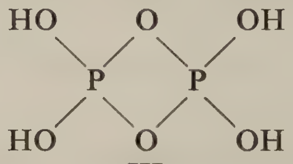
In 1894 Bansa[50] accepted the double formula and the symmetrical structure II because he was unable to form isomeric sodium and potassium salts.

The double formula agreed with conductivity and transport number measurements,[51] depression of the freezing point of aqueous solutions of sodium, potassium and ammonium hypophosphates[52] and the rate of hydrolysis of hypophosphates in acid solution.[53-4]

On the other hand some measurements of the elevation of the boiling point of ethyl iodide, ethyl bromide and chloroform by dissolved methyl hypophosphate appeared to show that the single formula was the correct one.[55] The same observations were found with solutions of the methyl ester in methyl iodide, the ethyl ester in ethyl iodide[56] and of the benzyl ester in diethyl ether.[57] However, the esters used for the molecular weight measurements were made by reaction of silver hypophosphate with the appropriate organic iodide, and later work has shown[58] that this method of preparation is not valid for hypophosphates, even though it is valid for the corresponding pyrophosphates. Silver halides react with organic hypophosphates to form addition compounds and organic iodides, e.g. ethyl iodide, cause hypophosphate esters to rearrange and form pyrophosphate[59-60]:



A re-examination of the rate of hydrolysis of hypophosphate in acid solution[49] confirmed the earlier findings[53] supporting the double formula. Further evidence in favour of this was provided in 1933 by measurements of the magnetic susceptibility of $Na_2H_2P_2O_6,6H_2O$, $Na_2H_2P_2O_6,Ag_4P_2O_6$ and guanidine hypophosphate. At 20°C. the respective values were found to be $-0{\cdot}41\times10^{-6}$, $-0{\cdot}38\times10^{-6}$, $-0{\cdot}41\times10^{-6}$ and $-0{\cdot}25\times10^{-6}$. The salts are therefore all diamagnetic and must be derived from an acid of the formula $H_4P_2O_6$. The $H_2PO_3$ molecule would have an odd number of electrons surrounding the phosphorus atom in the outer valency shell.[61] Structure III,

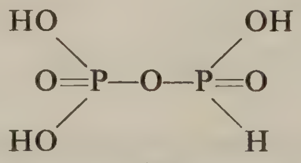


III

like the $H_2PO_3$ molecule, also has an odd number of electrons round each phosphorus atom. Both of them can therefore be rejected since such compounds would be paramagnetic.[62]

When non-electrolytes are added to ice–salt mixtures a normal molecular lowering of the eutectic point temperature is observed. The addition of electrolytes, however, gives a molecular lowering of the temperature which is proportional to the number of ions formed, other than common ions. When disodium hypophosphate or tetrapotassium hypophosphate is used in this technique the observed molecular lowering agrees with the formulæ $Na_2H_2P_2O_6$ and $K_4P_2O_6$.[63]

*X*-Ray absorption measurements on hypophosphoric acid and its sodium and barium salts strongly supported the symmetrical structure II. This also agreed with the tetra-basicity of the acid, its resistance to oxidation by nitric acid and the halogens, and with cryoscopic measurements.[64] On the other hand the ease of oxidation of hypophosphate to pyrophosphate by bromine at pH 5–11 favoured structure I, III or IV,



IV

of which I was considered to be the most probable.[65] However, although this oxidation could not be readily explained by a symmetrical acid containing a P–P bond, structure II was generally favoured at this time.[66–8]

Raman spectra of the free acid and its dipotassium salt showed too many lines for the monomeric formula $H_2PO_3$, and showed also that more complex units must be present. Although the experimental results agreed more closely with a dimeric formula, they were insufficient to establish structure II completely.[69] A later examination[9] showed the presence of a P–P bond and the absence of a P–H link. The $P_2O_6^{4-}$ ion comprised two equal $PO_3$ pyramids joined by a P–P bond, the $PO_3$ groups being staggered at an angle of 60° to each other. The six oxygen atoms were found to be equivalent.

*X*-Ray exmination of diammonium hypophosphate gives unit cell dimensions of $a=7{\cdot}26$, $b=11{\cdot}47$ and $c=9{\cdot}38$ A. Only structure II agrees with the data.[70] The unit cell size and space-group symmetry of the hypophosphate ion are very similar to those of ammonium bicarbonate.[71]

The di-, tri- and tetra-sodium salts of hypophosphoric acid are all monoclinic and each has four molecules in the unit cell. The trisodium salt has space group $P2_1/a$ and the other two are $C2/c$. The cell dimensions are given in Table III.[72]

*Table III.—The Cell Dimensions of Sodium Hypophosphates*[72]

| Salt | Cell dimensions—A. | | |
|---|---|---|---|
| | *a* | *b* | *c* |
| $Na_2H_2P_2O_6,6H_2O$ | 14·12 | 7·00 | 12·71 |
| $Na_3HP_2O_6,9H_2O$ | 26·96 | 6·00 | 9·26 |
| $Na_4P_2O_6,10H_2O$ | 16·97 | 6·97 | 14·50 |

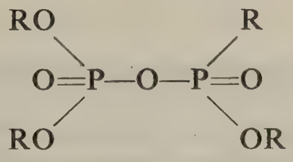
Infra-red absorption spectra in the 650 to 4000 cm.$^{-1}$ region have been tabulated for the sodium, ammonium, calcium, strontium, barium and lead hypophosphates.[73] Far ultra-violet absorption spectra of hypophosphates have been recorded.[110]

Nuclear magnetic resonance studies prove that structure II is the only possible one for hypophosphate. Only one resonance peak is shown and there is no evidence for P–H bonds. If the molecule contains two phosphorus atoms it must therefore have a symmetrical structure.[74]

By the same technique structure IV is the only one possible for isohypophosphoric acid.[75] The N.M.R. diagram is shown in Section XX, Fig. 2, p. 604. Peaks 1A and 1B in this are due to the P–H bond and peak 2 corresponds to the phosphorus atom which has no hydrogen atom directly attached to it.

Equations have been derived which enable the calculation of the A translations for the conditions $J_{XX'}=0$. Using these, the $^1H$ and $^{31}P$ spectra of the tetramethyl and tetraethyl esters of hypophosphoric acid were calculated, and shown to be in good agreement with observation.[103]

Chromatographic and Raman spectra data agree with the above structure for isohypophosphate.[34] Raman spectra also show that the structure of alkyl isohypophosphates is:



where R is an alkyl group.[76]

**Refs. p. 662**

## THE PROPERTIES OF HYPOPHOSPHORIC ACID AND THE HYPOPHOSPHATES

### Thermal Decomposition

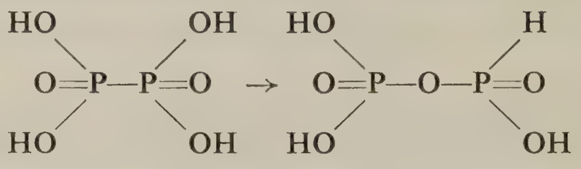
Hypophosphoric acid exists as an anhydrous material, and as a mono- and dihydrate. The melting points of these have been given as 70°C., 79·5° to 81·5°C. and 62° to 62·5°C. respectively. However, careful observation of the melting process shows that these are not true melting points. Rapid heating of the anhydrous acid gives an apparent m.p. of 55°C., but on slow heating, the melting temperature can vary between 70° and 95°C. The residue from the melting consists of phosphorous acid and a polymetaphosphoric acid, indicating the decomposition:

$$H_4P_2O_6 \rightarrow H_3PO_3 + \frac{1}{n}(HPO_3)_n$$

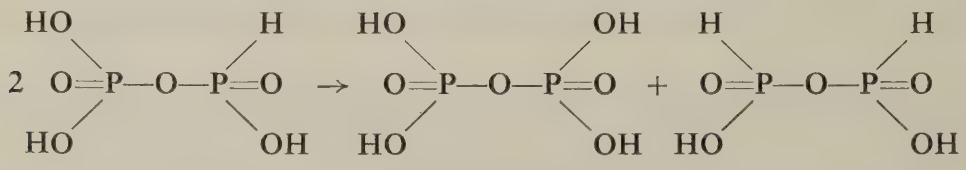
The dihydrate shows an apparent m.p. at 62° to 64°C., but on heating for 15 min. at 65°C. considerable decomposition into phosphoric and phosphorous acid occurs[9]:

$$H_4P_2O_6,2H_2O \rightarrow H_3PO_4 + H_3PO_3 + H_2O$$

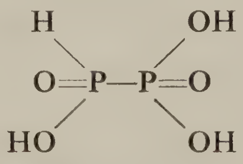
The dihydrate is stable for at least 2 months at −15°C.[9] but slowly decomposes at room temperature to become a clear liquid in 1–2 months. The anhydrous acid changes in 5 days to a viscous liquid which solidifies, but does not crystallize, at low temperature.[77] The final products of the spontaneous decomposition of hypophosphoric acid in the presence of water are phosphorous and phosphoric acids. However, a number of intermediate acids have been detected and under anhydrous conditions it appears that the first stage in the decomposition is the isomerization of hypophosphoric acid to isohypophosphoric acid[34–5,78]



Oxidation and reduction can then occur, leading to the formation of pyrophosphoric and pyrophosphorous acid:



Hypophosphorous acid $H_3PO_2$ and diphosphorous acid



have not been detected in this decomposition.[78]

### Hydrolysis and Oxidation

Hypophosphoric acid is very stable in alkaline solutions and is not hydrolyzed by heating for 1 hr. at 200°C. in 80–90% sodium hydroxide. In 80% potassium hydroxide solution less than 5% hydrolysis occurs on heating for 40 hr. at 200°C. Molten sodium hydroxide oxidizes, rather than hydrolyzes, hypophosphoric acid. At 320°C. in 30 min. a quantitative conversion to orthophosphate occurs. Hydrogen, but no phosphine, is evolved[24]:

$$H_4P_2O_6 + 6NaOH \rightarrow 2Na_3PO_4 + 4H_2O + H_2$$

In acid solutions the hydrolysis of hypophosphate is catalyzed by hydrogen ions, the rate of reaction being much slower than that for pyrophosphate or other polyphosphates under similar conditions. The products of the hydrolysis are phosphorous and phosphoric acids. Some data for the hydrolysis of $Na_2H_2P_2O_6,6H_2O$ in sulphuric acid solutions are given in Table IV.[49]

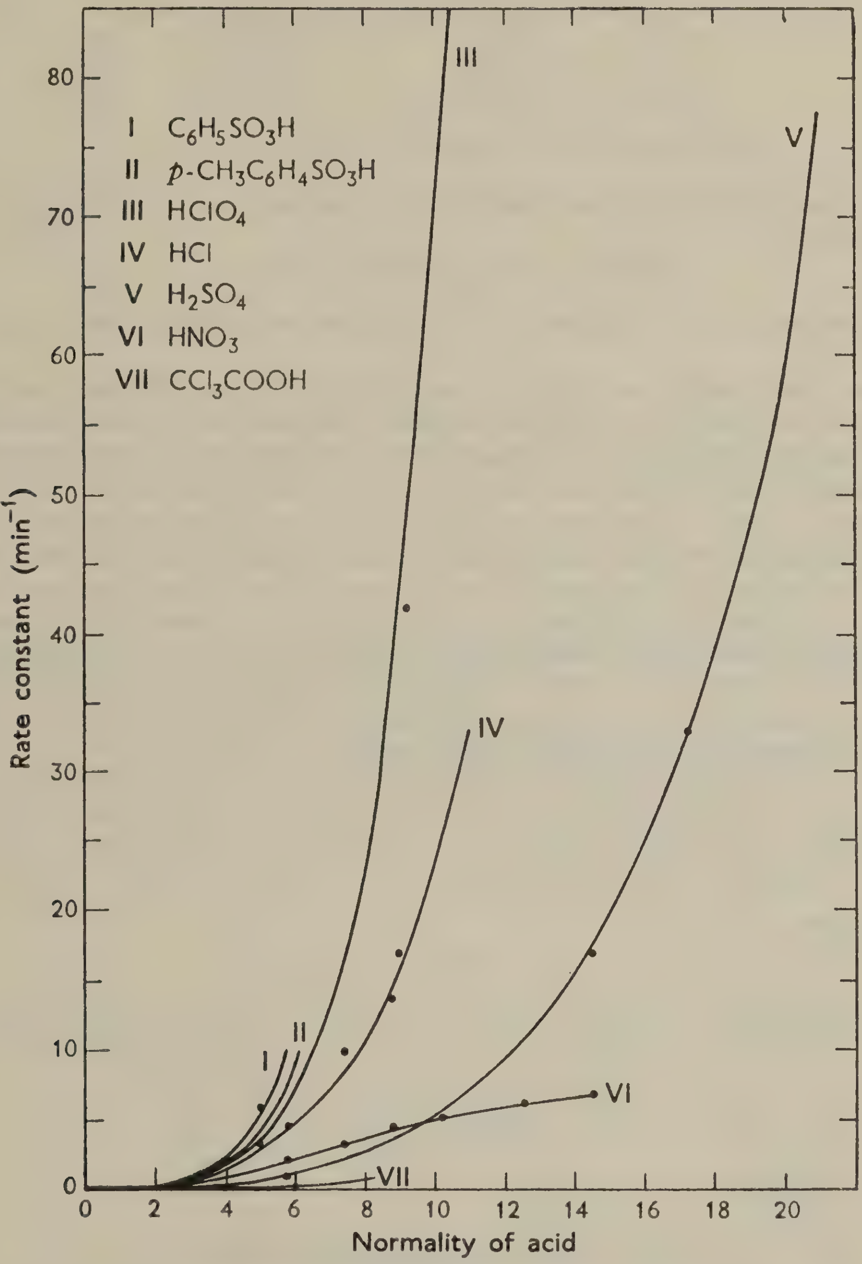


FIG. 1.—Hydrolysis of disodium hypophosphate in concentrated acid solutions[79]

At 25°C. in N.-acid solution the half-life is estimated to be approximately 180 days, i.e. $k = 2{\cdot}7 \times 10^{-6}$ min.$^{-1}$. These data are consistent with an activation energy of 20–25 kcal. mole$^{-1}$ for the hydrolysis in N.-acid solutions.[75] The first order rate constants for isohypophosphoric acid are $1{\cdot}4 \times 10^{-2}$ min.$^{-1}$ in 0·2 N. hydrochloric acid at 0°C.[35], $2\times10^{-4}$ min.$^{-1}$ in 0·5 N. potassium hydroxide at 0°C.[36] and $5{\cdot}4\times10^{-3}$ min.$^{-1}$ in N. sodium hydroxide at 34°C.[35]

Measurements of the rate of hydrolysis at 40°C. of $Na_2H_2P_2O_6{,}6H_2O$ in concentrated solutions of strong acids show that the reaction is of first order. The relevant data are shown graphically in Fig. 1, from which nitric acid is seen to be much less effective than the other mineral acids.[79] This acid has virtually no oxidizing action on hypophosphates. It behaves like the other acids as a hydrogen ion catalyst for the reaction[80]:

*Table IV.—Hydrolysis of Disodium Hypophosphate in Sulphuric Acid Solution*[49]

| Temp. °C. | Normality of $H_2SO_4$ | Rate constant min.$^{-1}$ |
|---|---|---|
| 60 | 0·5 | $1{\cdot}18\times10^{-4}$ |
| 60 | 1·0 | $2{\cdot}51\times10^{-4}$ |
| 100 | 0·25 | $4{\cdot}30\times10^{-3}$ |
| 100 | 0·50 | $6{\cdot}80\times10^{-3}$ |

$$H_4P_2O_6 + H_2O \rightarrow H_3PO_3 + H_3PO_4$$

The phosphorous acid is oxidized only if nitrogen oxides are present in the nitric acid.[81]

Reference has already been made to the stability of hypophosphoric acid towards oxidation by the halogens, hydrogen peroxide and acid solutions of potassium dichromate and potassium permanganate (Mellor, VIII, 930–1). The material appears to be oxidized slowly in cold acid solutions and more rapidly when hot, but this is not a direct oxidation to pyrophosphate. This is shown by the action of iodates, which have virtually no effect on hypophosphates in neutral or alkaline solution. In strong acid solutions the reaction is slow in the cold, but is complete in a few hours at 100°C. The initial action is one of hydrolysis which proceeds with a measurable velocity, and is followed by a rapid oxidation of phosphorous to phosphoric acid.[82]

The rate of reaction with 0·001 N. potassium permanganate in 0·1 N. sulphuric acid at 80°C. varies with the hypophosphate concentration as shown in Fig. 2; maximum velocity occurs at 0·015 M. $Na_2H_2P_2O_6$.[83]

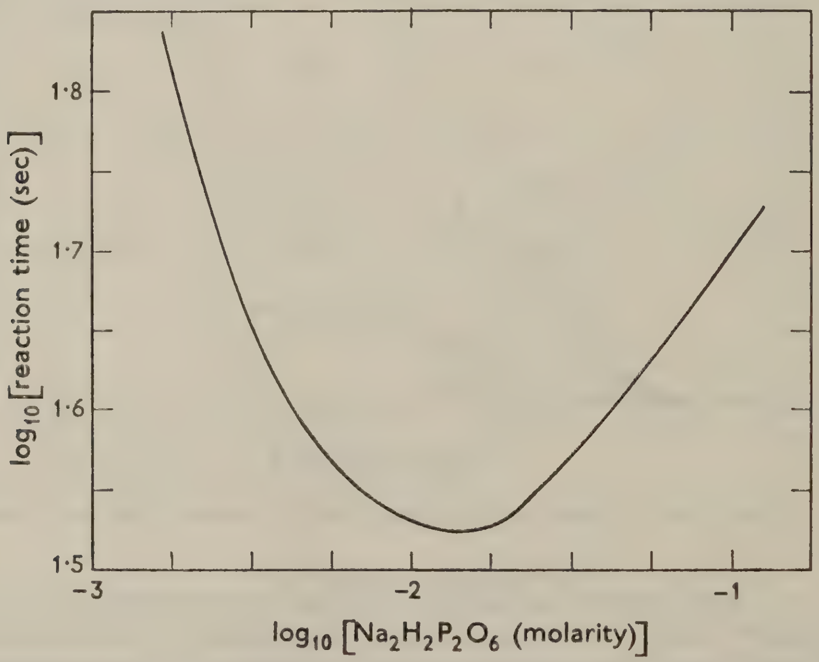


FIG. 2.—Rate of reaction of $Na_2H_2P_2O_6$ with 0·001 N. $KMnO_4$ at 80°C.

Bromine is one of the few reagents which oxidize hypophosphate directly to pyrophosphate without intermediate hydrolysis. The tetrasodium salt reacts according to the following equation[41]:

$$Na_4P_2O_6 + Br_2 + H_2O \rightarrow Na_2H_2P_2O_7 + 2NaBr$$

For the other sodium salts and the free acid the rate of oxidation depends on the pH, as shown in Fig. 3. The data for this were obtained by measuring the extent of oxidation by 0·1 N. aqueous bromine in 1 min. at 25°C. In the presence of excess of sodium bicarbonate at 20°C., the oxidation is at least 98% complete in 15 min. Less than 0·5% of orthophosphate is formed.[65]

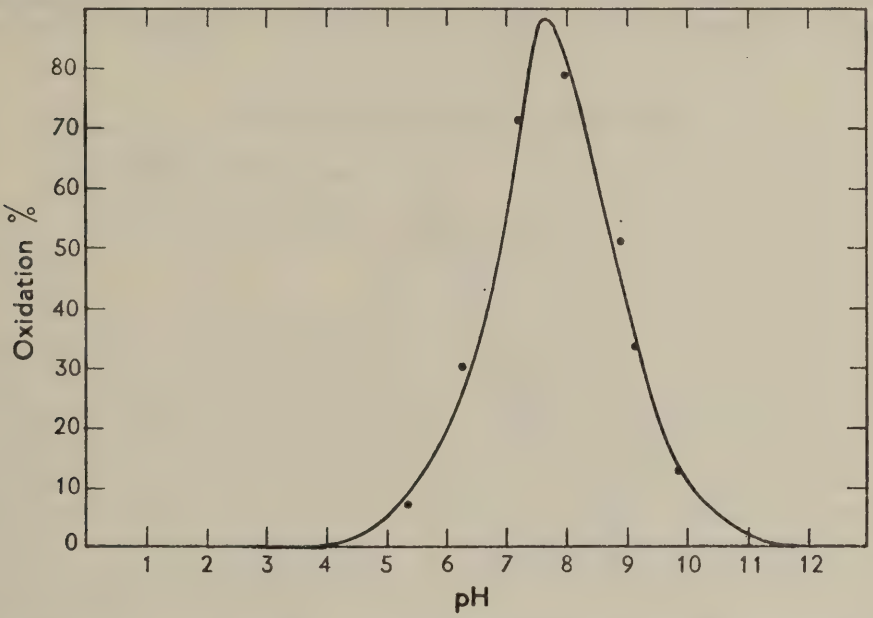


FIG. 3.—Effect of pH on the oxidation of hypophosphoric acid by 0·1 N.-$Br_2$ (aq.) at 25°C.[65]

More recently[3] a calculation of the variation in the hypobromous acid concentration with pH indicates that this is the oxidizing agent in the reaction. Fig. 4 shows the hypobromous acid concentration superimposed on the oxidation curve. The calculated values are based on the value $2{\cdot}1 \times 10^{-9}$ for the ionization constant of hypobromous acid[84] and the value $5{\cdot}8 \times 10^{-9}$ for the hydrolysis of bromine according to the equation[85]:

$$Br_2 + H_2O \rightleftharpoons HBrO + H^+ + Br^-$$

Bromite appears to be less effective as an oxidizing agent. A mechanism postulated for the hypobromite oxidation is[3]:

$$HP_2O_6^{3-} + HBrO \rightarrow 2PO_3^- + Br^- + H_2O$$
$$2PO_3^- + H_2O \rightarrow H_2P_2O_7^{2-}$$

## Dissociation and Solubilities in Water

The ionization constants of hypophosphoric acid have been given as $K_1 = 10^{-2{\cdot}2}$, $K_2 = 10^{-2{\cdot}81}$, $K_3 = 10^{-7{\cdot}27}$ and $K_4 = 10^{-10{\cdot}03}$, the first value being approximate. More recent values are $K_2 = 10^{-2{\cdot}1}$, $K_3 = 10^{-6{\cdot}77}$ and $K_4 = 10^{-9{\cdot}48}$ at 20°C.[87] These were obtained by electrometric titration using a hydrogen electrode in 0·10 N. potassium chloride solution. For comparison the results obtained in this way for pyrophosphoric acid gave $K_2 = 10^{-2{\cdot}5}$, $K_3 = 10^{-6{\cdot}08}$ and $K_4 = 10^{-8{\cdot}45}$.

Some solubility data for the ammonium, lithium, sodium, potassium, calcium, magnesium and hydrazine salts of hypophosphoric acid have been recorded previously (Mellor, VIII, 931–40). A more recent determination of the solubility diagrams for tetrasodium, trisodium and disodium hypophosphate shows that the tetrasodium salt undergoes an inversion of solubility at 66·5°C. This is interpreted as a change in the stable phase from $Na_4P_2O_6,10H_2O$ at low temperatures to the anhydrous salt above 66·5°. The trisodium salt $Na_3HP_2O_6,9H_2O$ shows a similar inversion at 58·5°C. and the disodium salt $Na_2H_2P_2O_6,6H_2O$ an inflection at 80·5°C. corresponding to a similar phase change to the anhydrous salts.[109] At 20°C., 48 g. of monoammonium hypophosphate, $NH_4H_3P_2O_6$, dissolve in 100 ml. of water.[9]

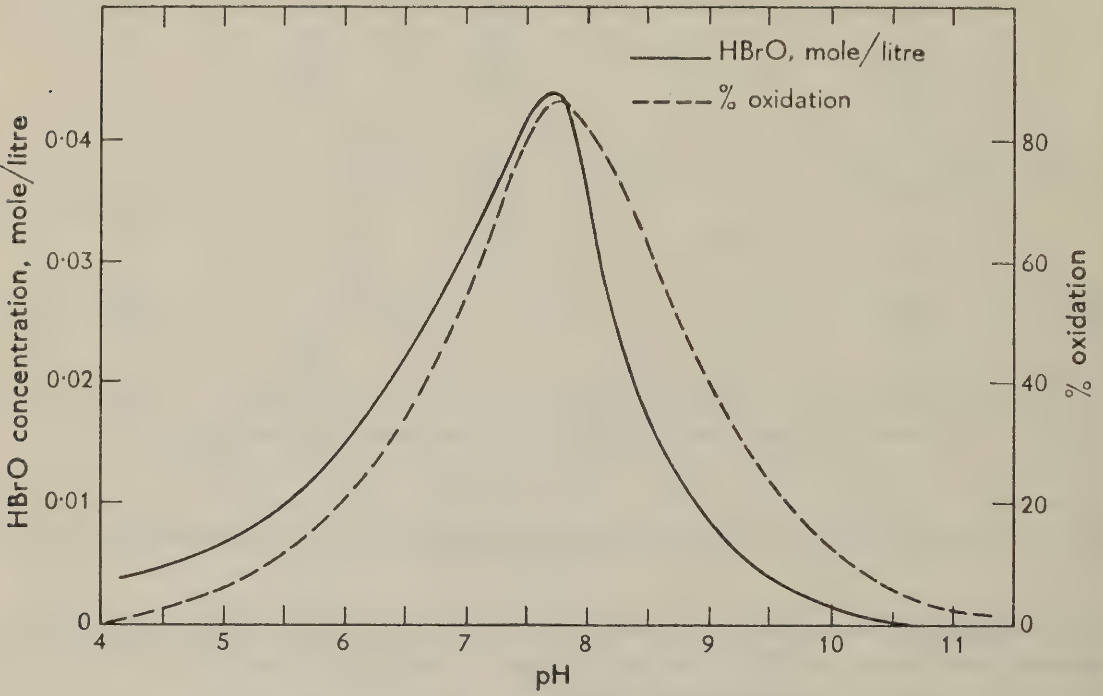


FIG. 4.—Oxidation of hypophosphate by hypobromite. (*cf.* Fig. 3)

The solubilities of the thorium, neodymium and yttrium salts in hydrochloric acid solutions at 25°C. are given in Table V.[47] The data for thorium hypophosphate agree with the figure of $0{\cdot}41 \times 10^{-4}$ mol./l. previously given for the solubility of $ThP_2O_6,11H_2O$ in N. hydrochloric acid (Mellor, VIII, 939).

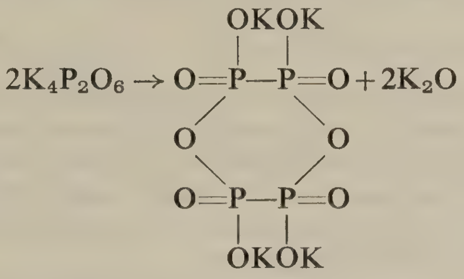
*Table V.—The Solubilities of Thorium, Neodymium and Yttrium Hypophosphates in Hydrochloric Acid Solutions at 25°C.*[47]

| HCl normality | Solubility (mol./l.) | | |
|---|---|---|---|
| | $ThP_2O_6$ | $Nd_4(P_2O_6)_3$ | $Y_4(P_2O_6)_3$ |
| 0·05 | — | $0{\cdot}11 \times 10^{-4}$ | — |
| 0·10 | — | $0{\cdot}48 \times 10^{-4}$ | — |
| 0·20 | — | $1{\cdot}60 \times 10^{-4}$ | $3{\cdot}02 \times 10^{-4}$ |
| 0·30 | — | $2{\cdot}0 \times 10^{-4}$ | $5{\cdot}52 \times 10^{-4}$ |
| 1·0 | $0{\cdot}25 \times 10^{-4}$ | $14{\cdot}46 \times 10^{-4}$ | $26{\cdot}90 \times 10^{-4}$ |
| 2·0 | $0{\cdot}47 \times 10^{-4}$ | $34{\cdot}7 \times 10^{-4}$ | — |
| 4·0 | $1{\cdot}65 \times 10^{-4}$ | — | — |
| 6·0 | $2{\cdot}10 \times 10^{-4}$ | — | — |

### Other Chemical Reactions of Hypophosphates involving conversion to other Phosphorous Acids

Several reactions involving hypophosphates have been referred to above. Those discussed below show the relationship between hypophosphoric acid and the other reduced acids of phosphorus which are described in more detail in Section XX (page 596).

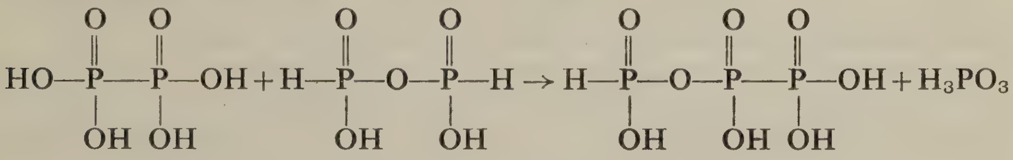
Tetrapotassium hypophosphate when heated with acetic anhydride for 40 hr. at 90°C. is converted to the potassium salt of the cyclic acid $(\overset{4}{P}\text{–}\overset{4}{P}\text{–}O)_2$



Somewhat higher yields are obtained in 68 hr. at 90°C. using a mixture of equal weights of propionic acid and propionic anhydride. The product is separated as the dihydrated guanidine salt, from which the sodium salt, $Na_4P_4O_{10},4H_2O$, is obtained by successive reaction with silver nitrate and sodium chloride. The sodium salt is also formed by heating disodium hypophosphate with a mixture of acetic acid and acetic anhydride, but separation from the unchanged hypophosphate is more difficult.[88] Properties of the material are given in Section XX. The free acid is monobasic and when heated at 150°C. with 60% potassium hydroxide it is quantitatively converted to hypophosphate.

Reaction with 1·5 N. sodium hydroxide at room temperature for a few hours converts the sodium salt into the sodium salt of the acid $\overset{4}{P}\text{–}\overset{4}{P}\text{–}O\text{–}\overset{4}{P}\text{–}\overset{4}{P}$. The latter is hydrolyzed by 0·2 N. nitric acid at 20°C. to give hypophosphoric acid. The first order rate constant for this reaction is $13{\cdot}3 \times 10^{-3}$ min.$^{-1}$

Hypophosphates react in aqueous solution with pyrophosphites to form salts of the acid $\overset{3}{P}\text{–}O\text{–}\overset{4}{P}\text{–}\overset{4}{P}$ by a process of trans-anhydrization. Under suitable conditions the yield is almost quantitative, but the rate of reaction depends on the temperature and on the concentration and pH of the solution[36].



$$HO\text{—}\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}\text{—}\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}\text{—}OH + H\text{—}\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}\text{—}O\text{—}\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}\text{—}H \rightarrow H\text{—}\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}\text{—}O\text{—}\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}\text{—}\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}\text{—}OH + H_3PO_3$$

Oxidation of the sodium salt of the $\overset{3}{P}\text{–}O\text{–}\overset{4}{P}\text{–}\overset{4}{P}$ acid by bromine in sodium bicarbonate solution converts it into equimolar proportions of ortho- and pyro-phosphate and the sodium salt of the $\overset{5}{P}\text{–}O\text{–}\overset{4}{P}\text{–}\overset{4}{P}$ acid.

$$Na_4HP_3O_8 + NaHCO_3 + O_2 \rightarrow Na_2HPO_4 + Na_3HP_2O_7 + CO_2$$
$$2Na_4HP_3O_8 + 2NaHCO_3 + O_2 \rightarrow 2Na_5P_3O_9 + 2CO_2 + 2H_2O$$

In N. $HNO_3$ or in 0·5 N. KOH the salt $Na_5P_3O_9$ is hydrolyzed to phosphorous and hypophosphoric acids:

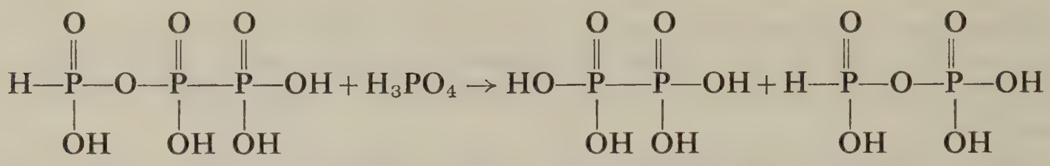
$$H_5P_3O_8 + H_2O \rightarrow H_4P_2O_6 + H_3PO_3$$

In concentrated acid the hypophosphate is further hydrolyzed to phosphite and phosphate:

$$H_5P_3O_8 + 2H_2O \rightarrow 2H_3PO_3 + H_3PO$$

**Refs. p. 662**

The salt $Na_4HP_3O_8$ reacts with orthophosphate to form hypophosphate and isohypophosphate[36]:



$$\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH + H_3PO_4 \rightarrow HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH + H{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH}$$

Tetrapotassium hypophosphate gives a 10% yield of $K_5P_3O_9$ on reaction with potassium phosphoramidate in 5 N. HBr (aq.) at 45°C. for 4 days:

$$K_4P_2O_6 + KHPO_3.NH_2 \rightarrow K_5P_3O_9 + NH_3$$

A 4% yield is also obtained by reaction of phosphorus oxychloride with a solution of potassium hypophosphate in the presence of excess potassium bicarbonate. The free acid ($H_5P_3O_9$) and its salts behave in a manner similar to $H_5P_3O_8$ during hydrolysis; in concentrated alkali or in dilute acid, orthophosphate and hypophosphate are formed, and in concentrated acid the hypophosphate is hydrolyzed further to phosphite and orthophosphate.[89]

The main reactions involving hypophosphoric acid are shown in Fig. 5.

## THE ANALYSIS OF HYPOPHOSPHATES

Several methods of analyzing hypophosphates have been reported and these are fully described in Section XXXV (page 1273).

For the sodium salts in the absence of other oxidizable phosphorus compounds, the simplest procedure is oxidation with 0·01 N. or 0·1 N. bromine solution in the presence of sodium bicarbonate. The excess bromine is then determined iodimetrically.[65]

Another method is to heat for 1 hr. with potassium iodate dissolved in 40% sulphuric acid solution. The iodine formed is distilled into potassium iodide solution, which is then titrated with standard arsenite solution.[3]

Hypophosphate can be determined in the presence of reduced acids of phosphorus by dissolving it in 0·5 N. nitric acid and precipitating with silver nitrate solution. The insoluble silver salt is collected, dried at 100°C. and then heated to bring about the decomposition:

$$Ag_4P_2O_6 \rightarrow 2Ag + 2AgPO_3$$

The residue is then weighed. Tetrametaphosphate and linear polyphosphates of chain length greater than tripolyphosphate interfere in this method.[3]

In the presence of hypophosphite, phosphite and phosphate it is an advantage to add a cold, saturated solution of barium nitrate to the hypophosphate solution. The precipitate is collected, washed and dissolved in 10% v/v phosphoric acid solution. Excess of standard silver nitrate solution is then added and after filtration the excess silver in the filtrate is titrated with standard potassium thiocyanate solution.[90-1]

If other reducing agents are absent, hypophosphates can be determined by adding 0·1 N. ceric ammonium nitrate solution and concentrated nitric acid. The solution is boiled until the initial precipitate dissolves, and is then cooled. The excess cerium(IV) is then titrated with standard arsenite solution, in the presence of a trace of osmic acid as a catalyst[92]:

$$P_2O_6^{4-} + 2Ce^{4+} + 2H_2O \rightarrow 2PO_4^{3-} + 2Ce^{3+} + 4H^+$$

Oxidation and hydrolytic reactions can be used to distinguish between hypophosphoric acid and isohypophosphoric, pyrophosphorous and diphosphorous acids: iodine in bicarbonate solution at room temperature oxidizes only the diphosphite.[23] Under the same conditions, bromine slowly oxidizes pyrophosphite[93] and isohypophosphate,[35] but rapidly oxidizes diphosphite[23] and hypophosphate[54] to pyrophosphate. The rates of hydrolysis are different for the four acids. In dilute acid

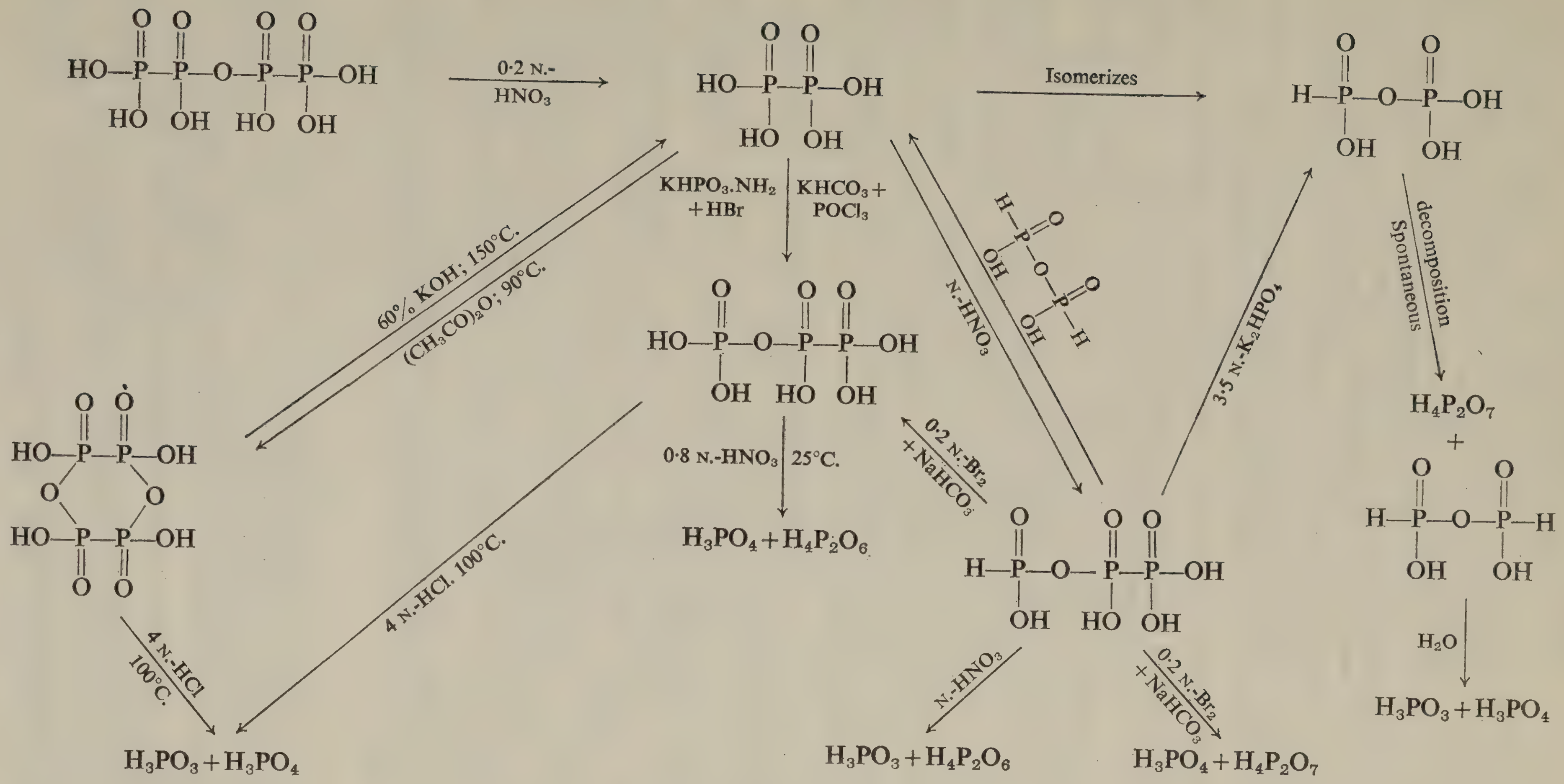


FIG. 5.—Reactions involving hypophosphoric acid

(0·2–0·5 N. HCl) pyrophosphite is hydrolyzed rapidly, with a half life of about 1 min. at 25°C., to form two molecules of phosphite.[36,94] Isohypophosphate forms one molecule each of phosphite and phosphate and the hydrolytic half-life is about 50 min. at 0°C.[89] Diphosphite hydrolyzes to two molecules of phosphite at a rate about 7–10 times slower than pyrophosphite.[22–3] Hypophosphoric acid is much more stable to hydrolysis and has a half-life of about 180 days in N. hydrochloric acid at 25°C.[49,53–4] Hypophosphates are extremely stable under alkaline conditions[24] while isohypophosphate has a half-life of about 440 min. in 0·1 N. sodium hydroxide at room temperature.[36] Diphosphite is not appreciably hydrolyzed in 1 hr. by boiling 2 N. sodium hydroxide[22] whereas pyrophosphite has a half-life of about 2 min. in the 0·1 N. alkali.[36]

Hypophosphates have been distinguished from the more recently discovered lower oxyacids of phosphorus by procedures similar to those described above.

Hypophosphoric acid and the cyclic acid $(\overset{4}{P}\text{–}\overset{4}{P}\text{–}O)_2$ are both completely hydrolyzed by boiling for 1 hr. in 4 N. hydrochloric acid. The $(\overset{4}{P}\text{–}\overset{4}{P}\text{–}O)_2$ acid, however, differs in not being oxidized by bromine in sodium bicarbonate solution. It also forms a barium salt which is insoluble in dilute hydrochloric acid.[88] The $\overset{4}{P}\text{–}\overset{4}{P}\text{–}O\text{–}\overset{4}{P}\text{–}\overset{4}{P}$ acid has similar properties which distinguish it from the hypophosphates.[88]

These three acids can be determined in the presence of one another by stirring with a solution containing sodium acetate and barium chloride. The mixture is then hydrolyzed for 1 hr. at room temperature in 2 N. hydrochloric acid, and the barium salt of $(\overset{4}{P}\text{–}\overset{4}{P}\text{–}O)_2$ is removed by centrifuging. This is now hydrolyzed at 100°C. in 4 N. HCl and oxidized with iodine in sodium bicarbonate solution. Similar treatment of the filtrate gives the sum of the hypophosphate and $\overset{4}{P}\text{–}\overset{4}{P}\text{–}O\text{–}\overset{4}{P}\text{–}\overset{4}{P}$. The hypophosphate content is obtained by oxidizing the original material with bromine and sodium bicarbonate.[36,88]

Oxidation methods for the determination of hypophosphate in the presence of phosphite and hypophosphite have been described.[95]

An electrometric titration procedure using a sulphuric acid solution of uranic sulphate in an atmosphere of carbon dioxide is reported to be a good method of determining hypophosphoric acid.[86,96]

An almost complete separation of ten acids of phosphorus, including hypophosphoric acid, has been achieved by paper chromatography.[97,104] For an acid solvent [$iso\text{-}C_3H_7OH + CCl_3COOH + H_2O + d\,0{\cdot}880\ NH_3(75+3:1+25+0{\cdot}3$ v/v)] the $R_f$ value for the hypophosphate is 0·48 and for a basic solvent [$C_2H_5OH + iso\text{-}C_4H_9OH + H_2O + d\,0{\cdot}880\ NH_3(30+30+39+1$ v/v)] the value is 0·21.[98] Thin layer chromatography has also been used to separate these acids.[105–6] Conditions for the development of colours from the anions by Mo(V)/ (VII) reagent have been established.[107–8]

Traces of copper, zinc, iron and tin in hypophosphates have been detected by electro-deposition on platinum wire electrodes using an applied potential of between 1 and 8 volts.[99]

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## SECTION XXIV

# THE PREPARATION OF ORTHOPHOSPHORIC ACID

BY J. E. SUCH

## ORTHOPHOSPHORIC ACID, $H_3PO_4$

### Preparation

SOLUTIONS of chemically pure orthophosphoric acid can be conveniently prepared in the laboratory by the action of dilute nitric acid on white phosphorus, or by the cautious hydrolysis of purified phosphorus oxychloride with distilled water. Both of these methods have been described in detail previously,[1] but, as then, it is scarcely worth following them since extremely pure orthophosphoric acid is readily available commercially.

On the industrial scale, preparation is commonly carried out by either of two methods. The more modern procedure is to burn phosphorus in an excess of air, followed by the hydration of the phosphoric oxide so formed with water or steam, according to the equations:

$$P_4+5O_2 = P_4O_{10}$$
$$P_4O_{10}+6H_2O = 4H_3PO_4$$

In some plants the phosphoric oxide is collected and hydrated separately; in others it is hydrated in the equipment in which the combustion stage also proceeds. Acid of any phosphoric oxide concentration up to 84% $P_2O_5$ (see Section XXVI) may be prepared by this technique, the usual grade being orthophosphoric acid of 75–85% strength (expressed as $H_3PO_4$).

Such commercial orthophosphoric acid is quite pure, containing no more than traces of the lower oxyacids of phosphorus, nor, after simple treatment to remove arsenic, of other impurities. A typical analysis of acid produced by the so-called thermal process is given in Table I.

*Table I.—Typical Analysis of Orthophosphoric Acid Produced by the Thermal Process*

| | |
|---|---|
| $H_3PO_4$ | 85·0% |
| $Fe_2O_3$ | 15 p.p.m. |
| $As_2O_3$ | 1·0 p.p.m. |
| F | <2 p.p.m. |
| $H_2SO_4$ | 18 p.p.m. |
| Pb | 2·0 p.p.m. |
| Cl | 10–20 p.p.m. |
| Ni | <1 p.p.m. |
| Cr | <1 p.p.m. |
| Cu | <1 p.p.m. |

The second, and somewhat older, method of preparing orthophosphoric acid is the treatment of rock phosphate with sulphuric acid. Calcium sulphate (gypsum, $CaSO_4,2H_2O$), silica and other insoluble matter are filtered off to yield an impure solution of orthophosphoric acid which, after further purification to remove fluorine compounds, sulphate and other impurities, can be subsequently concentrated. For some industrial applications, such as the manufacture of phosphatic fertilizers, or technical grade sodium and other metal phosphates, acid of this quality is satisfactory, but the elaborate and often expensive purification procedures which are necessary to achieve the quality required for the manufacture of food and pharmaceutical grade phosphates set a limit to the use of the so-called gypsum or wet-process orthophosphoric acid. A typical analysis of such acid is given in Table II.

*Table II.—Typical Analysis of Orthophosphoric Acid produced by the Gypsum Process*

| | % by wt. | | % by wt. |
|---|---|---|---|
| $P_2O_5$ | 29·9 | $V_2O_5$ | 0·024 |
| CaO | 0·36 | $U_3O_8$ | 0·016 |
| $Fe_2O_3$ | 0·19 | MgO | 0·29 |
| $Al_2O_3$ | 0·17 | $Na_2O$ | 0·19 |
| $Cr_2O_3$ | 0·036 | $SO_3$ | 0·78 |
| $SiO_2$ | 0·70 | F | 1·26 |

A very extensive literature (including many patent specifications) has developed during the past three decades on the technology of the thermal and gypsum processes for the production of orthophosphoric acid; useful bibliographies may be found in reviews[2, 46-7] and technical monographs.[3, 40, 42-3] A fuller account of this technology appears in Section II.

The simultaneous formation of orthophosphoric acid and hydrogen, by the reaction between phosphorus vapour and steam, first described in 1924 by Liljenroth,[4] has since been the subject of many other patents. This process, although lately developed on a pilot plant scale, has not so far developed industrially. The main reaction represented by the equation:

$$P_4+16H_2O = 4H_3PO_4+10H_2$$

has been studied between:

(*a*) phosphorus vapour and steam at high temperatures (800–2000°C.) and at atmospheric pressure, alone or in the presence of catalysts to lower the temperature for effective reaction, and

(*b*) liquid white, or solid red phosphorus and water at relatively low temperature (below 500°C.) as well as at superatmospheric pressure (up to 300 atm.), with and without catalysts.

Under some conditions (1000°C. under atmospheric pressure and in the absence of catalysts), both phosphorous acid and phosphine are formed in addition to orthophosphoric acid and hydrogen.[5-6] On the other hand, high conversions of phosphorus into substantially pure orthophosphoric acid and hydrogen can be obtained at atmospheric pressure by passing mixtures of steam and phosphorus vapour, in mol. ratios of 16:30, over copper or palladium catalysts at 650–800°C.[7-8] The reaction of water at lower temperatures under superatmospheric pressures with white[9-11] and red[12] phosphorus gives products which are generally contaminated with phosphorous acid and phosphine.

The mechanism and thermodynamics of this reaction have been considered more fully in Section V.

The formation of orthophosphoric acid and hydrogen by a similar process from metallic phosphides has also been reported.[13-4] The acid is also formed by the thermal decomposition of ammonium hypophosphite,[48] or the anodic oxidation of white phosphorus.[49]

Other rather more indirect methods have been suggested for the commercial preparation of orthophosphoric acid, such as heating tricalcium orthophosphate with sodium chloride, chlorine or phosgene, followed by aqueous hydrolysis of the phosphorus oxychloride produced in the initial reaction.

Substitutes for sulphuric acid in the usual method of attacking phosphate rock have been reported; for example, hydrochloric acid,[15-6] hydrofluoric acid,[17] and mixtures of sulphurous and hydrochloric acids.[18-9]

Solvent extraction is often recommended as a method of separating and purifying orthophosphoric acid made by these and other processes which do not rely on the formation and filtration of insoluble calcium salts. Many solvents have been suggested for this purpose, including aliphatic alcohols,[20-1, 44] ketones,[22-3] esters,[24, 41] and ethers.[17] Of twenty-four different solvents studied, alcohols were found to be the best for extracting orthophosphoric acid from aqueous solutions, followed by ketones and ethers[25-6]; the theory of the solvent extraction process has also been discussed.[26, 45] The preparation of phosphoric acid by the attack of acids upon phosphate rock, and its purification by solvent extraction are discussed in greater detail in Section II (page 72 *et seq.*).

### Purification

Commercial orthophosphoric acid can be purified by recrystallization from solution as the anhydrous acid[27-8] or as the hemihydrate, $H_3PO_4,\frac{1}{2}H_2O$.[29] Heavy metal or metalloid impurities may be deposited electrolytically using chromium, platinum or tantalum electrodes[30-1] and to assist in the removal of traces of arsenic by this method additions of copper salts are sometimes made.[32-4] Arsenic may also be removed by passing acid containing it over copper foil,[35] or by treating the acid with sodium or hydrogen sulphide and filtering off the precipitated arsenic trisulphide, $As_2S_3$.[40] The precipitation of metallic impurities can also be brought about by the treatment of dilute orthophosphoric acid with several volumes of glacial acetic acid.[36]

## "HEAVY" ORTHOPHOSPHORIC ACID, $D_3PO_4$

"Heavy" orthophosphoric acid (deuterophosphoric acid, $D_3PO_4$), has been prepared in several ways[37-9]:

(*a*) by the addition of phosphoric oxide to heavy water, $D_2O$,
(*b*) by the hydrolysis of phosphorus oxychloride with heavy water, and
(*c*) by the decomposition of barium orthophosphate with heavy sulphuric acid, $D_2SO_4$,

the most convenient method being the first.

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## SECTION XXV

# THE PHYSICAL AND CHEMICAL PROPERTIES OF ORTHOPHOSPHORIC ACID

BY J. E. SUCH

## PHYSICAL PROPERTIES

### The System $P_2O_5$–$H_2O$

THE solubility phase diagram for the system $P_2O_5$–$H_2O$, up to and including compositions corresponding to pyrophosphoric acid, shown in Fig. 1 is based on currently available data[1–6] (see also Ref. 234).

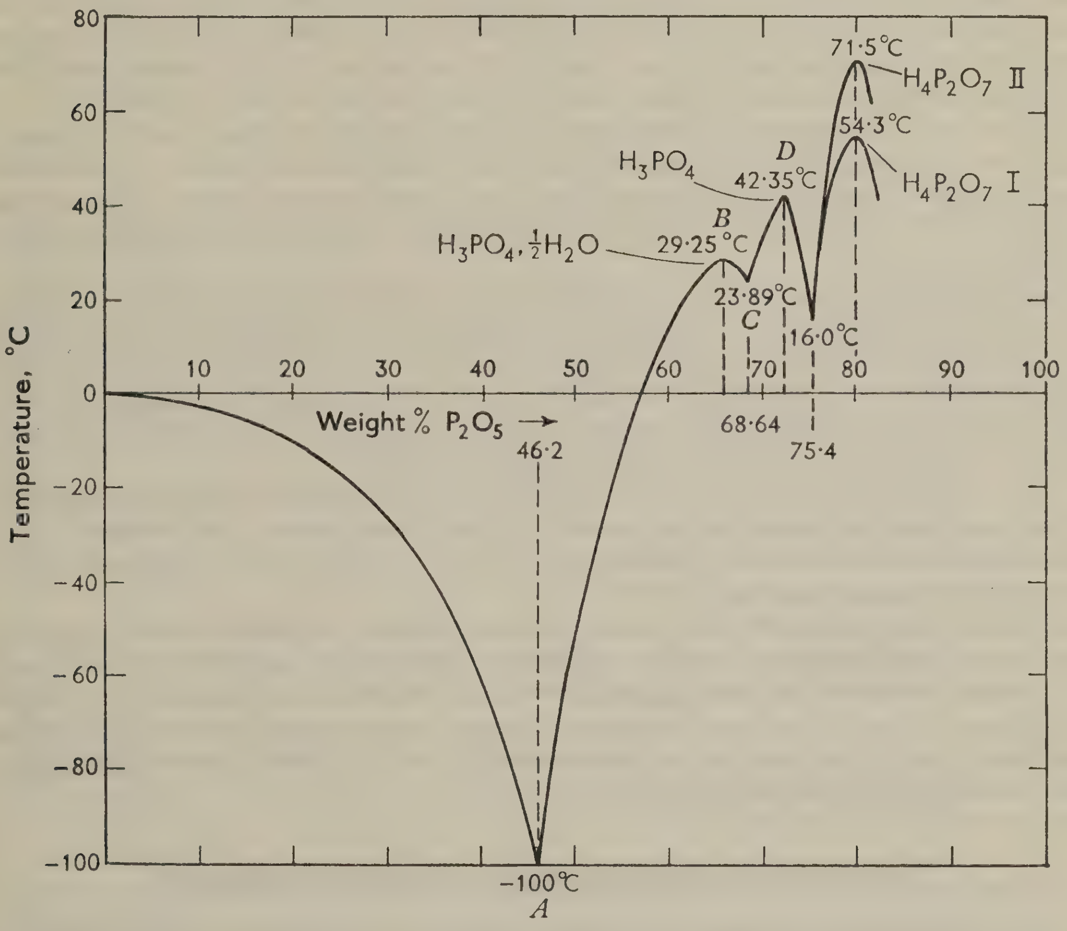


FIG. 1.—Solubility phase diagram of the system $P_2O_5$–$H_2O$

The solid crystalline phases in the orthophosphoric region of the system are the anhydrous acid $H_3PO_4$, m.p. 42·35°C., and the hemihydrate $H_3PO_4,\frac{1}{2}H_2O$, m.p. 29·25°C.

When anhydrous orthophosphoric acid crystals are rapidly melted and the temperature is observed before rearrangement in the liquid phase occurs according to the equilibrium[2,4-6]:

$$2H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O$$

freezing-point values approximating to those noted by Ross and Jones,[1] viz. 42·35°C., are obtained. If, however, the anhydrous acid is maintained in the molten condition, the freezing point gradually falls to an equilibrium value of 34·6°C. after about 3 weeks; this temperature corresponds to the presence of about 6 mole-% of pyrophosphoric acid.[4] Thus slow melting of anhydrous crystals in contact with a liquid phase that has had the opportunity to approach equilibrium with other species of phosphoric acid may lead to lower values than 42·35°C.[5,6]

Solid $H_3PO_4$ exists in equilibrium with solutions of different concentrations of $P_2O_5$ at temperatures shown by that section of the curve between the melting point *D* and the eutectic point *C*.

Curve *CBA* shows the temperatures at which the solution is in equilibrium with the hemihydrate as the solid phase. The lowering of the melting point of the hemihydrate is represented by the section of the curve *BC*, *C* being the eutectic point (23·89°C. and 68·64% $P_2O_5$) at which the anhydrous and hemihydrated acids co-exist as solid phases with the solution.

Section *BA* represents the lowering of the melting point of the hemihydrate down to the second eutectic point *A*, at which this hydrate, ice and the solution co-exist. The most recent investigation places this point at −100°C. and 46·2% $P_2O_5$,[3] i.e. at a temperature somewhat lower than that previously reported,[1] but not inconsistent with the experimental data quoted therein. Observations of the freezing points at these low temperatures are difficult owing to the extreme viscosity prevailing.

Evidence for a hydrate $10H_3PO_4,H_2O$ was first obtained by Smith and Menzies,[7] but its existence could not be confirmed by later phase diagram studies[1,8]; however, small changes in the slope of the electrical conductivity–composition curves in this region, at 25°C., are claimed to indicate the presence of a hydrate with the composition quoted above.[8]

Pure orthophosphoric acid supercools readily; in the absence of nuclei, or agitation, acid corresponding in composition to the hemihydrate (91·6% $H_3PO_4$), which normally solidifies at 29·25°C., can be stored without crystallization for long periods at temperatures 10–20°C. below the melting point. Slow rates of crystallization have been reported[1] for supercooled orthophosphoric acids, e.g. 2·6 cm./min. in a horizontal tube at 22°C. for $H_3PO_4,\frac{1}{2}H_2O$, and confirmed.[9]

The transition temperature from the glassy to the liquid state in highly supercooled dilute solutions containing 0·5–10 mole-% $H_3PO_4$ was found to be −114°C. from differential thermal analysis measurements,[10] and −121°C. from a discontinuity in conductivity measurements.[11]

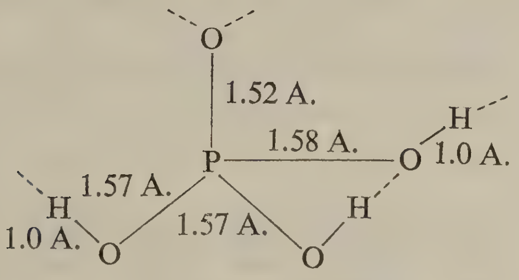
It has been suggested[12] from a study of the physical properties, such as specific heat, molal heat capacity, density, electrical conductivity and dielectric constant of aqueous solutions of orthophosphoric acid, that liquid hydrates are present which have ordered structures, with a preferential arrangement of solvent and solute molecules. For $H_3PO_4$, liquid hydrates with 0·5, 1, 4, 8, 12 and 28 molecules of water per mole of solute have been proposed.

## The Structure of Orthophosphoric Acid and its Hemihydrate

*X*-Ray diffraction studies have established that orthophosphoric acid molecules in the crystalline and liquid states of both the anhydrous and hemihydrated compounds contain $PO_4$ groups in which the oxygen atoms are arranged tetrahedrally around the central phosphorus atom[13-7]; a similar conclusion follows from Raman spectroscopic studies of liquid phosphoric acid and its solutions in water.[18-23] The Raman data, together with the infra-red spectra of $PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^{-}$,

$H_3PO_4$ and their deuterated analogues, have been assigned on the basis of a regular change of symmetry through the series $PO_4^{3-}(T_d)$, $HPO_4^{2-}$ (pseudo-$C_{3v}$), $H_2PO_4^-$ ($C_{2v}$ or lower), and $H_3PO_4$ (lower than pseudo-$C_{3v}$).[335] Urey–Bradley–Simanouti force constants have been calculated for the ions and the free acid, and discussed in relation to P–O bond orders.[336]

Investigations in all these fields have indicated that hydrogen bonding plays an important part in the structures of the crystalline and liquid forms of the acid. For example, three of the oxygen atoms of the $PO_4$ groups in the anhydrous acid are hydrogen-bonded to oxygen atoms in neighbouring $PO_4$ groups (see Fig. 2), whilst in the liquid or solution states hydrogen bonding occurs either to other $PO_4$ groups in the more concentrated acids (86% $H_3PO_4$) or to the water lattice at lower concentrations (54% $H_3PO_4$). Infra-red studies have shown an increased strength of hydrogen bonding in the sequence $HClO_4 < H_2SO_4 < H_3PO_4$, with a corresponding increase in the length of the OH bond, associated with a diminution in the bond force constant.[337]



--- = hydrogen bonds

FIG. 2.—The structure of orthophosphoric acid

The possible existence of ordered structures of liquid hydrates with a range of compositions has already been referred to.[12]

The structure of orthophosphoric acid hemihydrate has not been determined, although incomplete *X*-ray data have been published[14] which suggest that there are four formula weights per unit cell. Although the anhydrous acid and its hemihydrate have the same space group symmetry, it is not possible to deduce structural similarity from available *X*-ray data. However the study of the infra-red spectra of crystalline phosphoric acid and phosphoric acid hemihydrate in a low temperature cell disclosed the existence of a number of crystalline modifications as follows:

Phosphoric acid, cooled in liquid nitrogen or solid carbon dioxide, crystallizes to a glass, which on warming to −54°C. crystallizes to $H_3PO_4$-III. This is converted reversibly at −8° to −6°C., to $H_3PO_4$-I, which is stable at room temperature. A third phase, $H_3PO_4$-II, crystallizes from the melt between +8 and +15°C. if the latter has not been heated much above the melting point. $H_3PO_4$-II is stable if cooled down to −190°C., but when warmed up again is converted to $H_3PO_4$-I at −4° to 0°C.

The hemihydrate similarly forms a glass, which crystallizes at −54° to −49°C. to $H_3PO_4,\frac{1}{2}H_2O$-II. There is an irreversible transformation to $H_3PO_4,\frac{1}{2}H_2O$-I at −32° to −30°C., which is marked by a positive thermal effect, but produces little change in the spectrum.[338]

For a more detailed discussion of the structural chemistry of phosphoric acid see Section XXXIV.

## Density, Partial Molal Volume and Molecular Volume

### DENSITY

A self-consistent composition–density relation at 25°C. over the range 0 to 90% $H_3PO_4$ is represented by the four following equations[24]:

For 0–6% $H_3PO_4$

$$\bar{\rho} = (189{\cdot}5\sqrt{X}+5392{\cdot}0X)\times 10^{-6}$$
$$X = (\sqrt{185{\cdot}46\,\bar{\rho}+0{\cdot}0003088}-0{\cdot}01757)^2$$

For 5–90% $H_3PO_4$

$$\bar{\rho} = (5369{\cdot}1X+17{\cdot}913X^2+0{\cdot}21238X^3-0{\cdot}0005510X^4)\times 10^{-6}$$
$$X = (186{\cdot}3522\bar{\rho}-130{\cdot}8834\bar{\rho}^2+57{\cdot}6796\bar{\rho}^3)$$

where $\bar{\rho}$, the incremental density, is the density of the solution in g./ml., less 0·99707, the density of water at 25°C., and $X$ is the wt.-% of $H_3PO_4$.

The density equations are accurate to less than 1 part in 10,000, the corresponding errors in composition varying, nearly linearly, from just under 0·04% for the most dilute to just under 0·02% for the most concentrated solution.

The equations provide the data for Table I. Although the values quoted differ erratically from those given in International Critical Tables[25] by one or two units in the third decimal place of density, they are the most reliable yet available.

*Table I.—Density of Orthophosphoric Acid at* 25°C., g./ml.

| $H_3PO_4$ wt.-% | 0·0 | 0·1 | 0·2 | 0·3 | 0·4 | 0·5 | 0·6 | 0·7 | 0·8 | 0·9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0·9971 | 0·9977 | 0·9982 | 0·9988 | 0·9994 | 0·9999 | 1·0005 | 1·0010 | 1·0016 | 1·0021 |
| 1 | 1·0027 | 1·0032 | 1·0038 | 1·0043 | 1·0048 | 1·0054 | 1·0059 | 1·0065 | 1·0070 | 1·0076 |
| 2 | 1·0081 | 1·0086 | 1·0092 | 1·0097 | 1·0102 | 1·0108 | 1·0113 | 1·0119 | 1·0124 | 1·0130 |
| 3 | 1·0135 | 1·0141 | 1·0146 | 1·0152 | 1·0157 | 1·0163 | 1·0168 | 1·0174 | 1·0179 | 1·0184 |
| 4 | 1·0190 | 1·0196 | 1·0201 | 1·0207 | 1·0212 | 1·0218 | 1·0223 | 1·0229 | 1·0234 | 1·0240 |
| 5 | 1·0245 | 1·0251 | 1·0256 | 1·0262 | 1·0267 | 1·0273 | 1·0279 | 1·0284 | 1·0290 | 1·0295 |
| 6 | 1·0301 | — | — | — | — | — | — | — | — | — |
|  | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0 | 0·9971 | 1·0027 | 1·0081 | 1·0135 | 1·0190 | 1·0245 | 1·0301 | 1·0357 | 1·0413 | 1·0470 |
| 10 | 1·0528 | 1·0585 | 1·0644 | 1·0703 | 1·0763 | 1·0823 | 1·0884 | 1·0945 | 1·1006 | 1·1069 |
| 20 | 1·1132 | 1·1196 | 1·1260 | 1·1325 | 1·1390 | 1·1456 | 1·1523 | 1·1590 | 1·1658 | 1·1727 |
| 30 | 1·1796 | 1·1866 | 1·1937 | 1·2008 | 1·2080 | 1·2152 | 1·2226 | 1·2300 | 1·2375 | 1·2450 |
| 40 | 1·2527 | 1·2604 | 1·2682 | 1·2760 | 1·2840 | 1·2920 | 1·3002 | 1·3084 | 1·3166 | 1·3250 |
| 50 | 1·3334 | 1·3419 | 1·3505 | 1·3592 | 1·3679 | 1·3768 | 1·3857 | 1·3947 | 1·4038 | 1·4130 |
| 60 | 1·4223 | 1·4316 | 1·4411 | 1·4506 | 1·4603 | 1·4700 | 1·4799 | 1·4898 | 1·4999 | 1·5100 |
| 70 | 1·5202 | 1·5305 | 1·5409 | 1·5514 | 1·5620 | 1·5727 | 1·5834 | 1·5943 | 1·6052 | 1·6163 |
| 80 | 1·6275 | 1·6387 | 1·6500 | 1·6614 | 1·6729 | 1·6845 | 1·6961 | 1·7079 | 1·7198 | 1·7317 |
| 90 | 1·7438 | 1·7561 | — | — | — | — | — | — | — | — |

Measurements of the density of aqueous solutions of orthophosphoric acid have also been made at 15°–80°C.[26] Equations fitted to the data (overall deviation in representing the density 0·2 mg./ml.) gave the smoothed densities and density–temperature coefficients in Table II.

Other data[8] at 0°, 25° and 50°C. for orthophosphoric acid ranging in concentration from 0·38 to 98·5% $H_3PO_4$ are in fair agreement with those quoted in Table II. Values have also been recorded at temperatures up to 200°C.[339]

A useful nomograph giving the wt.-% of $H_3PO_4$ and the density of aqueous solutions at temperatures from 15° to 80°C. has been constructed.[28]

The density isotherms at 25°, 45°, 75° and 95°C. of $H_2SO_4$–$H_3PO_4$–$H_2O$ solutions at 33, 52, 63 and 73 wt.-% concentrations of $H_3PO_4+H_2SO_4$ have been determined. They are not linear, but slightly convex towards the composition axis.[340] The temperature dependence of density at equal concentrations is however nearly linear, and is given by the equation

$$\rho_t = \rho_{25}-\alpha(t-25)$$

Table II.—Smoothed Densities and Density-temperature Coefficients of Orthophosphoric Acid Solutions, g./ml.

| $H_3PO_4$ wt.-% | 15°C. | | 25°C. | | 40°C. | | 60°C. | | 80°C. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\rho$ | $\frac{d\rho}{dt} \times 10^5$ | $\rho$ | $\frac{d\rho}{dt} \times 10^5$ | $\rho$ | $\frac{d\rho}{dt} \times 10^5$ | $\rho$ | $\frac{d\rho}{dt} \times 10^5$ | $\rho$ | $\frac{d\rho}{dt} \times 10^5$ |
| 0 | 0·9991 | | 0·9971 | | 0·9922 | | 0·9832 | | 0·9718 | |
| 5 | 1·0268 | 23 | 1·0241 | 29 | 1·0189 | 39 | 1·0097 | 52 | 0·9977 | 64 |
| 10 | 1·0553 | 29 | 1·0523 | 34 | 1·0468 | 43 | 1·0373 | 53 | 1·0247 | 64 |
| 15 | 1·0852 | | 1·0819 | | 1·0759 | | 1·0661 | | 1·0531 | |
| 20 | 1·1165 | 32 | 1·1129 | 38 | 1·1065 | 46 | 1·0963 | 58 | 1·0829 | 69 |
| 25 | 1·1493 | | 1·1453 | | 1·1385 | | 1·1280 | | 1·1142 | |
| 30 | 1·1837 | 39 | 1·1794 | 45 | 1·1721 | 53 | 1·1611 | 63 | 1·1472 | 74 |
| 35 | 1·2198 | | 1·2151 | | 1·2074 | | 1·1960 | | 1·1818 | |
| 40 | 1·2577 | 53 | 1·2527 | 56 | 1·2444 | 62 | 1·2326 | 68 | 1·2183 | 76 |
| 45 | 1·2974 | | 1·2920 | | 1·2834 | | 1·2710 | | 1·2566 | |
| 50 | 1·3391 | 56 | 1·3334 | 59 | 1·3242 | 62 | 1·3114 | 67 | 1·2969 | 72 |
| 55 | 1·3828 | | 1·3767 | | 1·3672 | | 1·3539 | | 1·3392 | |
| 60 | 1·4287 | 62 | 1·4223 | 64 | 1·4122 | 67 | 1·3985 | 71 | 1·3836 | 75 |
| 65 | 1·4768 | | 1·4700 | | 1·4596 | | 1·4453 | | 1·4303 | |
| 70 | 1·5271 | 73 | 1·5200 | 73 | 1·5092 | 74 | 1·4945 | 75 | 1·4792 | 75 |
| 75 | 1·5798 | | 1·5725 | | 1·5613 | | 1·5462 | | 1·5305 | |
| 80 | 1·6350 | 76 | 1·6275 | 77 | 1·6159 | 78 | 1·6003 | 78 | 1·5843 | 80 |
| 85 | 1·6928 | | 1·6850 | | 1·6732 | | 1·6572 | | 1·6406 | |
| 90* | 1·7532 | 80 | 1·7452 | 80 | 1·7331 | 81 | 1·7168 | 82 | 1·6996 | 83 |
| 95* | 1·8163 | | 1·8082 | | 1·7959 | | 1·7792 | | 1·7612 | |
| 100* | 1·8823 | 83 | 1·8741 | 84 | 1·8616 | 84 | 1·8446 | 85 | 1·8257 | 86 |

* Extrapolated.

where $\rho_t$ and $\rho_{25}$ are the densities at temperatures $t$ and 25°C. respectively, and $\alpha$ varies from $8{\cdot}2 \times 10^{-4}$ in $H_3PO_4$ rich to $10{\cdot}4 \times 10^{-4}$ in $H_2SO_4$ rich solutions.[341]

PARTIAL MOLAL VOLUME

Calculated values[26-7] for the partial molal volume $\overline{V}_2$ of orthophosphoric acid and of the relative partial molal volume $-(\overline{V}_1 - V_1^\circ)$ of water in orthophosphoric acid solutions are given in Tables III and IV respectively.

*Table III.—Partial Molal Volume, $\overline{V}_2$ of $H_3PO_4$ in Orthophosphoric Acid Solutions, c.c./mole $H_3PO_4$*

| $H_3PO_4$ wt.-% | 15°C. | 25°C. | 40°C. | 60°C. | 80°C. |
|---|---|---|---|---|---|
| 10 | 46·64 | 47·12 | 47·77 | 48·26 | 49·16 |
| 20 | 47·47 | 47·92 | 48·52 | 49·09 | 49·63 |
| 30 | 48·28 | 48·68 | 49·23 | 49·80 | 50·20 |
| 40 | 49·08 | 49·43 | 49·91 | 50·48 | 50·83 |
| 50 | 49·85 | 50·16 | 50·59 | 51·14 | 51·52 |
| 60 | 50·57 | 50·84 | 51·24 | 51·75 | 52·18 |
| 70 | 51·19 | 51·43 | 51·81 | 52·30 | 52·78 |
| 80 | 51·66 | 51·90 | 52·25 | 52·74 | 53·26 |
| 90 | 51·96 | 52·18 | 52·54 | 53·03 | 53·57 |
| 100 | 52·06 | 52·29 | 52·64 | 53·13 | 53·68 |

*Table IV.—Relative Partial Molal Volume, $-(\overline{V}_1 - V_1^\circ)$ of $H_2O$ in Orthophosphoric Acid Solutions, c.c./mole $H_2O$*

| $H_3PO_4$ wt.-% | 15°C. | 25°C. | 40°C. | 60°C. | 80°C. |
|---|---|---|---|---|---|
| 10 | 0·0164 | 0·0099 | 0·0104 | 0·0115 | 0·0080 |
| 20 | 0·0434 | 0·0360 | 0·0347 | 0·0380 | 0·0235 |
| 30 | 0·0932 | 0·0827 | 0·0780 | 0·0820 | 0·0586 |
| 40 | 0·1730 | 0·1570 | 0·1462 | 0·1495 | 0·1222 |
| 50 | 0·2893 | 0·2675 | 0·2489 | 0·2491 | 0·2264 |
| 60 | 0·4517 | 0·4209 | 0·3948 | 0·3875 | 0·3756 |
| 70 | 0·6639 | 0·6233 | 0·5896 | 0·5761 | 0·5815 |
| 80 | 0·9247 | 0·8814 | 0·8347 | 0·8190 | 0·8477 |
| 90 | 1·2427 | 1·1827 | 1·1377 | 1·1161 | 1·1719 |
| 100 | 1·5825 | 1·5112 | 1·4900 | 1·4880 | 1·5014 |

MOLECULAR VOLUME

Extrapolated values for the density and molecular volume, $MV_0$, of orthophosphoric acid at −273°C. are given as 2·08 g./c.c. and 47·2 respectively.[29] Hence

$$\frac{MV_0}{n} = 11{\cdot}8$$

compared with 11·0 and 11·3 for sulphuric and nitric acids, and close to 10·9, the value of $MV_0$ for oxygen itself; $n$ equals the number of oxygen atoms in the molecule.

## Vapour Pressure

The vapour pressure of water over aqueous solutions of orthophosphoric, pyrophosphoric and other polyphosphoric acids has been studied by various methods over a wide range of composition and temperature. For example, measurements have been made by the static method of solutions containing 4·11–92·7% $P_2O_5$ at temperatures ranging from 25° to 866°C.[30-4]; by the isotonic method, calculated to activities, of solutions containing 1·2–63·7% $P_2O_5$ at 25°C.[35]; and by the dynamic method of solutions containing 62·7–79·6% $P_2O_5$ at 35°–280°C.[36]

The boiling points, at 1 atm., of solutions containing 9·1–92·7% of $P_2O_5$ have been observed[32–3, 37] and some measurements made of the composition of the vapour phase.[32, 38]

*Table V.—Vapour Pressure of Aqueous Orthophosphoric Acid*

| $H_3PO_4$ wt.-% | Constants in vapour pressure equations | | Vapour pressure in mm. Hg at indicated temperature °C. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | 25 | 40 | 50 | 60 | 75 | 80 | 100 |
| 1·60 | 2935·3 | 23·4260 | 23·64 | 55·0 | 92·0 | 149 | 287 | 352 | 749 |
| 4·49 | 2935·5 | 23·4242 | 23·50 | 54·7 | 91·5 | 148 | 285 | 350 | 746 |
| 8·14 | 2935·9 | 23·4220 | 23·30 | 54·3 | 90·7 | 146 | 283 | 347 | 739 |
| 13·63 | 2936·8 | 23·4181 | 22·94 | 53·4 | 89·3 | 144 | 279 | 342 | 731 |
| 16·69 | 2937·5 | 23·4159 | 22·71 | 52·9 | 88·5 | 143 | 276 | 339 | 722 |
| 20·07 | 2938·6 | 23·4135 | 22·39 | 52·2 | 87·3 | 141 | 272 | 335 | 713 |
| 23·06 | 2939·4 | 23·4111 | 22·12 | 51·6 | 86·3 | 139 | 269 | 331 | 705 |
| 29·80 | 2943·8 | 23·4092 | 21·29 | 49·7 | 83·3 | 135 | 261 | 320 | 684 |
| 35·06 | 2950·4 | 23·4133 | 20·43 | 47·8 | 80·2 | 130 | 252 | 310 | 663 |
| 39·18 | 2956·9 | 23·4170 | 19·59 | 46·0 | 77·2 | 125 | 243 | 299 | 642 |
| 45·49 | 2970·1 | 23·4243 | 18·00 | 42·4 | 71·5 | 116 | 227 | 279 | 602 |
| 50·20 | 2981·4 | 23·4275 | 16·61 | 39·3 | 66·4 | 108 | 212 | 261 | 565 |
| 55·35 | 2995·4 | 23·4243 | 14·80 | 35·2 | 59·7 | 97·6 | 192 | 237 | 515 |
| 60·59 | 3013·8 | 23·4170 | 12·63 | 30·3 | 51·5 | 84·5 | 167 | 207 | 452 |
| 63·87 | 3027·8 | 23·4078 | 11·10 | 26·7 | 45·6 | 75·1 | 149 | 185 | 406 |
| 65·07 | 3033·0 | 23·4021 | 10·52 | 25·4 | 43·4 | 71·5 | 142 | 176 | 388 |
| 67·64 | 3046·1 | 23·3944 | 9·34 | 22·6 | 38·8 | 64·1 | 128 | 159 | 351 |
| 70·90 | 3066·2 | 23·3837 | 7·80 | 19·1 | 32·8 | 54·5 | 109 | 136 | 303 |
| 73·82 | 3085·9 | 23·3692 | 6·48 | 15·9 | 27·6 | 46·0 | 92·9 | 116 | 259 |
| 75·26 | 3098·6 | 23·3680 | 5·86 | 14·5 | 25·1 | 42·0 | 85·2 | 106 | 239 |
| 77·81 | 3121·3 | 23·3448 | 4·66 | 11·6 | 20·3 | 34·0 | 69·4 | 86·8 | 197 |
| 80·14 | 3145·0 | 23·3422 | 3·86 | 9·7 | 17·0 | 28·7 | 59·0 | 73·9 | 170 |
| 84·88 | 3210·5 | 23·3315 | 2·27 | 5·8 | 10·4 | 17·8 | 37·3 | 47·0 | 110 |
| 87·99 | 3265·6 | 23·3335 | 1·49 | 3·9 | 7·1 | 12·2 | 26·1 | 33·0 | 78·8 |

Data for acids containing up to 87·99% $H_3PO_4$ (63·9% $P_2O_5$) have been correlated and tabulated,[39] the relevant portions being reproduced in Table V. The vapour pressures in Table V, calculated from equations of the form:

$$\log_{10} p_{\text{mm}} = -\frac{A}{T} - 4{\cdot}9373 \log T + 1{\cdot}639 \times 10^{-5}\, T + 4{\cdot}874 \times 10^{-8}\, T^2 + B$$

represent the data from which they were derived with a probable maximum error of 1%.

For solutions of higher concentration, including pyrophosphoric and polyphosphoric acid compositions, equations[32] based on the values quoted in Table VI may be used to calculate water–vapour pressures over solutions containing 61·6–92·7% $P_2O_5$.

Equations of the form:

$$\log_{10} p_{\text{mm}} = A - B/T$$

fit the data used for the compilation of Table VI with a maximum mean deviation of 3% in the temperature ranges quoted.

Two nomographs relating vapour pressures of orthophosphoric acid and concentrations have been presented,[40–1] of which the second is more useful since it covers a wider range of acid concentrations and is based on more complete data than the first.

The temperature–composition diagram for the complete system $P_2O_5$–$H_2O$ is described more fully in Section XXVI (page 734).

The vapour pressure of mixtures of aqueous orthophosphoric acid with nitric acid has been studied[42]; in contrast to the system $HNO_3$–$H_2SO_4$–$H_2O$, the total vapour pressure of the $HNO_3$–$H_3PO_4$–$H_2O$ system is a simple function of the nitric acid concentration[43] and there is evidence of only a slight tendency to form hydrates.

The vapours over mixtures of 100% nitric and 100% orthophosphoric acid contain no measurable excess of $H_2O$ or $N_2O_5$, from which it has been inferred that orthophosphoric acid cannot be greatly dehydrated in nitric acid solutions. Measurements at 0°C. of the partial pressure of the $HNO_3$ in a range of $H_3PO_4$–$HNO_3$ mixtures suggest that polymerization of $HNO_3$ rather than polyacid formation by elimination of water accounts for the observed results.[44]

*Table VI.—Constants in Vapour Pressure Equations for Phosphoric Acid Solutions containing* 61·6–92·7% $P_2O_5$ *and their b.p. at* 760 mm. Hg

| Concentration of acid expressed as | | Constants in vapour pressure equation | | Temperature range °C. | B.p. at 760 mm. |
|---|---|---|---|---|---|
| % $P_2O_5$ | % by wt. $H_3PO_4$ | A | B | | |
| 61·6 | 85·0 | 8·76803 | 2515 | 96–154 | 154·2 |
| 63·7 | 87·9 | 8·62745 | 2498 | 111–161 | 161·6 |
| 66·1 | 91·3 | 8·82154 | 2677 | 104–177 | 177·6 |
| 66·9 | 92·4 | 8·53453 | 2605 | 123–188 | 187·8 |
| 68·5 | 94·6 | 8·47185 | 2603 | 138–193 | 192·6 |
| 69·0 | 95·3 | 8·67564 | 2770 | 138–207 | 205·1 |
| 70·3 | 97·1 | 8·42196 | 2757 | 156–224 | 224·5 |
| 72·4 | 100·0 | 8·80520 | 3130 | 183–255 | 255·3 |
| 75·3 | 104·0 | 8·88389 | 3451 | 223–301 | 301·9 |
| 76·3 | 105·3 | 8·70453 | 3483 | 276–326 | 325·1 |
| 78·2 | 108·0 | 8·92487 | 3960 | 298–383 | 382·2 |
| 78·7 | 108·7 | 8·40933 | 3611 | 310–380 | 380·1 |
| 79·7 | 110·0 | 8·74361 | 4106 | 341–427 | 427·3 |
| 81·5 | 112·5 | 8·89940 | 4530 | 385–479 | 479·7 |
| 83·7 | 115·6 | 8·45125 | 4492 | 425–533 | 533·4 |
| 85·9 | 118·6 | 8·32016 | 4930 | 539–633 | 633·4 |
| 88·5 | 122·2 | 8·94513 | 6097 | 631–732 | 732·4 |
| 91·9 | 126·9 | 8·16863 | 5967 | 705–855 | 855·4 |
| 92·7 | 128·0 | 7·97852 | 5805 | 694–866 | 865·8 |

## Viscosity

The viscosities of aqueous orthophosphoric acid solutions reported from various earlier sources[45-8] have been smoothed by graphical methods to yield the data[39,49] given in Table VII.

The estimated accuracy of the tabulated values is:

±10% for 0–110% $H_3PO_4$ at 25°C.
±15% for 0–75% $H_3PO_4$ at all temperatures except 25°C.
±10% for 75–118% $H_3PO_4$ at all temperatures.

Other values[8,50] at 0°, 25° and 50°C. for orthophosphoric acids ranging from 0·38 to 98·5% $H_3PO_4$ agree fairly well with those quoted in Table VII.

The most recent data at 25°C.[51] are contained in Table VIII; they are in agreement, where they overlap, with some previous measurements[52] which were not available for the compilation quoted in Table VII, but for solutions more concentrated than 1 molal (8·9% $H_3PO_4$) the viscosities are from 0·7 to 2·0% higher than the values stated therein.

Table VII.—Kinematic Viscosity of Orthophosphoric Acid

| Concentration of acid expressed as | | Viscosity, centistokes at indicated temperature, °C. | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % by wt. $H_3PO_4$ | % $P_2O_5$ | 20 | 25 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 120 | 130 | 140 | 150 | 160 | 170 | 180 |
| 5 | 3·6 | 1·1 | 0·99 | 0·89 | 0·74 | 0·63 | 0·54 | 0·47 | 0·42 | 0·37 | 0·33 | | | | | | | | |
| 10 | 7·2 | 1·2 | 1·1 | 0·99 | 0·83 | 0·71 | 0·61 | 0·54 | 0·47 | 0·42 | 0·38 | | | | | | | | |
| 15 | 10·9 | 1·4 | 1·2 | 1·1 | 0·94 | 0·81 | 0·69 | 0·61 | 0·53 | 0·47 | 0·43 | | | | | | | | |
| 20 | 14·5 | 1·6 | 1·4 | 1·3 | 1·1 | 0·92 | 0·78 | 0·69 | 0·60 | 0·54 | 0·48 | | | | | | | | |
| 25 | 18·1 | 1·8 | 1·6 | 1·5 | 1·2 | 1·0 | 0·89 | 0·79 | 0·69 | 0·61 | 0·55 | | | | | | | | |
| 30 | 21·7 | 2·2 | 1·9 | 1·7 | 1·4 | 1·2 | 1·0 | 0·90 | 0·79 | 0·70 | 0·62 | | | | | | | | |
| 35 | 25·4 | 2·6 | 2·2 | 2·0 | 1·6 | 1·3 | 1·1 | 1·0 | 0·90 | 0·79 | 0·71 | | | | | | | | |
| 40 | 29·0 | 3·0 | 2·6 | 2·3 | 1·9 | 1·5 | 1·3 | 1·2 | 1·0 | 0·90 | 0·81 | | | | | | | | |
| 45 | 32·6 | 3·6 | 3·1 | 2·7 | 2·2 | 1·8 | 1·5 | 1·3 | 1·2 | 1·0 | 0·92 | | | | | | | | |
| 50 | 36·2 | 4·3 | 3·7 | 3·3 | 2·6 | 2·1 | 1·8 | 1·6 | 1·4 | 1·2 | 1·1 | | | | | | | | |
| 55 | 39·8 | 5·3 | 4·5 | 4·0 | 3·2 | 2·5 | 2·1 | 1·9 | 1·6 | 1·4 | 1·2 | 1·1 | | | | | | | |
| 60 | 43·5 | 6·6 | 5·6 | 5·0 | 3·9 | 3·1 | 2·5 | 2·2 | 1·9 | 1·7 | 1·4 | 1·3 | | | | | | | |
| 65 | 47·1 | 8·4 | 6·8 | 6·2 | 4·9 | 3·8 | 3·1 | 2·6 | 2·3 | 2·0 | 1·7 | 1·5 | 1·4 | | | | | | |
| 70 | 50·7 | 11 | 9·2 | 7·8 | 6·1 | 4·7 | 3·9 | 3·2 | 2·7 | 2·4 | 2·0 | 1·8 | 1·6 | | | | | | |
| 75 | 54·3 | 15 | 12 | 10 | 7·8 | 5·9 | 4·8 | 3·9 | 3·3 | 2·8 | 2·4 | 2·1 | 1·9 | 1·7 | | | | | |
| 80 | 57·9 | 20 | 17 | 14 | 10 | 7·6 | 6·2 | 4·9 | 4·1 | 3·4 | 3·0 | 2·6 | 2·3 | 2·0 | 1·8 | | | | |
| 85 | 61·6 | 28 | 23 | 19 | 14 | 10 | 8·1 | 6·3 | 5·1 | 4·2 | 3·8 | 3·2 | 2·8 | 2·4 | 2·2 | 1·9 | | | |
| 90 | 65·2 | 41 | 34 | 27 | 19 | 14 | 11 | 8·3 | 6·5 | 5·4 | 4·8 | 4·0 | 3·5 | 3·0 | 2·8 | 2·4 | 2·1 | | |
| 95 | 68·8 | 68 | 55 | 42 | 30 | 20 | 15 | 12 | 8·7 | 7·3 | 6·2 | 5·2 | 4·4 | 3·8 | 3·3 | 3·0 | 2·6 | 2·3 | 2·1 |
| 100 | 72·4 | 140 | 100 | 81 | 53 | 36 | 25 | 19 | 14 | 11 | 9·2 | 7·7 | 6·2 | 5·2 | 4·5 | 4·1 | 3·5 | 3·2 | 2·9 |
| 105 | 76·1 | 600 | 440 | 330 | 173 | 110 | 70 | 50 | 33 | 25 | 19 | 15 | 12 | 9·6 | 8·0 | 7·1 | 6·0 | 5·2 | 4·5 |
| 110 | 79·7 | — | 2200 | 1600 | 810 | 410 | 270 | 170 | 100 | 67 | 50 | 38 | 29 | 22 | 18 | 15 | 13 | 10 | 8·8 |
| 115 | 83·3 | — | — | — | — | — | 1500 | 1000 | 600 | 380 | 250 | 190 | 120 | 99 | 68 | 54 | 41 | 34 | 28 |
| 118 | 85·5 | — | — | — | — | — | — | — | 2000 | 1200 | 830 | 550 | 400 | 320 | 210 | 170 | 130 | 107 | 87 |

*Table VIII.—Dynamic Viscosity of Orthophosphoric Acid at* 25°C., *Centipoises*

| $H_3PO_4$ wt.-% | Viscosity | $H_3PO_4$ wt.-% | Viscosity |
|---|---|---|---|
| 0 | 0·8902 | 45 | 4·094 |
| 5 | 1·015 | 50 | 5·090 |
| 10 | 1·166 | 55 | 6·378 |
| 15 | 1·350 | 60 | 8·105 |
| 20 | 1·576 | 65 | 10·48 |
| 25 | 1·879 | 70 | 13·90 |
| 30 | 2·254 | 75 | 19·03 |
| 35 | 2·728 | 80 | 27·60 |
| 40 | 3·329 | | |

The average deviation of the values shown in Table VIII from observed viscosities is:

±0·15% for 2–21% $H_3PO_4$
±0·31% for 21–49% $H_3PO_4$
±0·77% for 49–83% $H_3PO_4$

The temperature dependence of the viscosity, $\eta$, of orthophosphoric acid has been discussed. The relationship between log $\eta$ and $1/T$ (absolute) is not linear,[53] neither is that between log $\eta/\eta_0$ and $1/T$ (absolute), except possibly for solutions containing less than 68% $H_3PO_4$ in the temperature range 25°–75°C.[50] The viscosity–composition isotherms of the $H_2SO_4$–$H_3PO_4$–$H_2O$ system also deviate from linearity,[340] the deviation becoming less at higher temperatures.[342]

A study of viscosities in the $P_2O_5$–$H_2O$ system at temperatures up to 200°C. showed a discontinuity at 130°–140°C., and a hysteresis effect below 80°, at around 72 wt.-% $P_2O_5$ ($\equiv H_3PO_4$). The viscosity returned to its original value overnight at room temperature. No similar discontinuity was shown by the $P_2O_5$–$SO_3$–$H_2O$ system, and $SO_3$ lowered the viscosity of the $P_2O_5$–$H_2O$ system. The activation energy for viscous flow of phosphoric acid solutions varied with concentration from 3·0 to 8·1 kcal./mole, showing a maximum in the region 100°–170°C. The results suggested that at high $P_2O_5$ concentrations and low temperatures phosphoric acid contains a hydrate and associated or condensed polymer systems.[343]

The relationship between the conductivity and viscosity of orthophosphoric acid solutions has also been studied; a linear correlation is said to exist between the logarithm of the specific resistance and the logarithm of the viscosity,[11] and a minimum has been noted at about 10% $H_3PO_4$ in the curve obtained when corrected conductivity, $(\lambda \times \eta/\eta_{H_2O})$, is expressed as a function of concentration.[50] The simple Falkenhagen formula[54] expressing the viscosity of electrolyte solutions as a function of concentration does not apply to 0·02–1·4 M. aqueous solutions of orthophosphoric acid at 25°C., but a modified formula, which considers the effect of association, is applicable.[52]

## Diffusion Coefficient

The concentration diffusion coefficient, $k$, corrected to 20°C., for aqueous solutions of orthophosphoric acid is reported[55] to be:

| Concentration $H_3PO_4$ | 0·25 N. | 1 N. | 2 N. | 3 N. |
|---|---|---|---|---|
| $k_{20}$ | 0·772 | 0·692 | 0·656 | 0·644 |

A later determination of the diffusion coefficient of aqueous orthophosphoric acid ($D$ in cm.$^2$ sec.$^{-1}$) shows that $D$ decreases from 0·036 to 1 M., remains roughly constant from 1 to 5 M. and then decreases again to 16 M. By extrapolation a value of $7{\cdot}6 \times 10^{-6}$ cm.$^2$ sec.$^{-1}$ is obtained for $D_m^\circ$, the hypothetical limiting diffusion coefficient for undissociated phosphoric acid at 25°.[302]

The thermal diffusion of orthophosphoric acid has also been investigated on the supposition that the velocity of thermal diffusion of the solute is accelerated by the presence of $H^+$ or $OH^-$ ions.[56]

Both the thermal and the concentration diffusion coefficients are smaller than those of strong acids, for example nitric or sulphuric acid, by a factor of about 3, consistent with the smaller degree of dissociation of orthophosphoric acid.

## Surface Tension and Parachor

Surface tension measurements[57, 18] (see Table IX) have been used to calculate the parachor[58] of 100% liquid orthophosphoric acid, and the value obtained denotes the presence of hydrogen bonding; concentrated nitric and sulphuric acids are also thought by the same reasoning to contain similar linkages.

*Table IX.—Surface Tension, $\gamma$, of Orthophosphoric Acid in dynes/cm.*$^2$

| °C. | $H_3PO_4$, wt.-% | | | |
|---|---|---|---|---|
| | 86·00 | 90·33 | 100* | 100·65 |
| 20 | 79·72 | 79·76 | 79·92 | 79·93 |
| 22·5 | 79·48 | 79·57 | 79·81 | 79·84 |
| 25·0 | 79·23 | 79·36 | 79·70 | 79·73 |
| 27·5 | 78·99 | 79·17 | 79·59 | 79·62 |
| 30·0 | 78·74 | 78·96 | 79·48 | 79·50 |

*Interpolated.

The parachor for 100% orthophosphoric acid calculated from these data is only 129·2, compared with the value of 169 obtained by adding together atomic parachors. This is indicative of association, the effect being greater than that shown, for example,

*Table X.—Relative Partial Molal Heat Content of Orthophosphoric Acid in Orthophosphoric Acid Solutions, $(\bar{H}_2 - \bar{H}_2^\circ)$, g.cal./mole* $H_3PO_4$

| $H_3PO_4$ wt.-% | 15° | 25° | 40° | 60° | 70° | 80° |
|---|---|---|---|---|---|---|
| 5 | 381 | 406 | 437 | 500 | 550 | 644 |
| 10 | 513 | 590 | 639 | 745 | 798 | 878 |
| 15 | 688 | 754 | 791 | 943 | 1036 | 1111 |
| 20 | 856 | 931 | 988 | 1126 | 1194 | 1252 |
| 25 | 1062 | 1151 | 1222 | 1353 | 1407 | 1475 |
| 30 | 1295 | 1392 | 1462 | 1580 | 1644 | 1741 |
| 35 | 1547 | 1651 | 1731 | 1852 | 1918 | 2016 |
| 40 | 1823 | 1929 | 2022 | 2161 | 2229 | 2329 |
| 45 | 2114 | 2229 | 2337 | 2490 | 2561 | 2652 |
| 50 | 2424 | 2549 | 2668 | 2845 | 2933 | 3030 |
| 55 | 2748 | 2889 | 3026 | 3220 | 3317 | 3419 |
| 60 | 3088 | 3247 | 3408 | 3626 | 3726 | 3842 |
| 65 | 3445 | 3619 | 3794 | 4025 | 4134 | 4259 |
| 70 | 3816 | 3998 | 4185 | 4433 | 4550 | 4685 |
| 75 | 4185 | 4374 | 4573 | 4841 | 4968 | 5108 |
| 80 | 4537 | 4733 | 4943 | 5221 | 5352 | 5495 |
| 85 | 4858 | 5059 | 5279 | 5568 | 5703 | 5849 |

by sulphuric acid. It should also be remembered that liquid orthophosphoric acid undergoes reorganization (see page 702) with the formation of other species of polyacids.

Two other values of the parachor have also been reported, 144·4 for 2·55 molar orthophosphoric acid and 154·7 for 15·87 molar acid; two intramolecular hydrogen bonds have been postulated from these data, in agreement with *X*-ray crystallographic and Raman spectra studies.[59]

*Table XI.—Relative Partial Molal Heat Content of Water in Orthophosphoric Acid Solutions,* $-(\bar{H}_1-\bar{H}_1^{\circ})$, *g.cal./mole* $H_3PO_4$

| $H_3PO_4$ wt.-% | 15° | 25° | 40° | 60° | 70° | 80° |
|---|---|---|---|---|---|---|
| 5 | 1·106 | 1·314 | 1·612 | 1·864 | 2·100 | 2·675 |
| 10 | 2·930 | 4·020 | 2·495 | 3·326 | 3·557 | 3·817 |
| 15 | 7·627 | 8·288 | 8·605 | 10·88 | 12·36 | 12·28 |
| 20 | 13·97 | 15·35 | 16·76 | 18·47 | 18·49 | 18·03 |
| 25 | 25·33 | 27·15 | 28·78 | 29·86 | 29·53 | 29·87 |
| 30 | 41·54 | 43·92 | 45·55 | 45·37 | 45·75 | 47·89 |
| 35 | 64·00 | 66·91 | 69·41 | 69·83 | 70·38 | 72·64 |
| 40 | 94·70 | 97·74 | 102·0 | 105·3 | 106·0 | 108·4 |
| 45 | 133·1 | 138·5 | 144·6 | 149·4 | 150·8 | 152·2 |
| 50 | 185·8 | 191·9 | 199·6 | 208·1 | 212·0 | 214·3 |
| 55 | 252·1 | 261·3 | 272·8 | 285·5 | 290·9 | 294·4 |
| 60 | 336·5 | 350·6 | 368·3 | 385·8 | 392·5 | 399·8 |
| 65 | 446·6 | 464·9 | 486·7 | 508·3 | 517·4 | 527·0 |
| 70 | 588·3 | 610·0 | 636·6 | 664·9 | 677·5 | 690·1 |
| 75 | 767·7 | 792·7 | 824·8 | 862·6 | 880·1 | 896·0 |
| 80 | 991·7 | 1021 | 1060 | 1104 | 1123 | 1142 |
| 85 | 1271 | 1305 | 1352 | 1406 | 1428 | 1450 |

*Table XII.—Relative Partial Molal Free Energy of Orthophosphoric Acid in Orthophosphoric Acid Solutions,* $(\bar{F}_2-\bar{F}_2^{\circ})$, *g.cal./mole* $H_3PO_4$

| $H_3PO_4$ wt.-% | 15° | 25° | 40° | 60° | 70° | 80° |
|---|---|---|---|---|---|---|
| 5 | −430·1 | −458·5 | −502·4 | −563·4 | −595·6 | −629·8 |
| 10 | 81·16 | 64·67 | 36·70 | −4·94 | −28·37 | −53·94 |
| 15 | 415·6 | 404·9 | 386·4 | 356·7 | 337·8 | 316·1 |
| 20 | 693·8 | 686·6 | 672·5 | 647·9 | 632·1 | 614·2 |
| 25 | 950·9 | 945·4 | 933·2 | 911·1 | 897·0 | 881·1 |
| 30 | 1204 | 1199 | 1187 | 1166 | 1152 | 1136 |
| 35 | 1464 | 1459 | 1447 | 1425 | 1411 | 1395 |
| 40 | 1741 | 1736 | 1724 | 1701 | 1686 | 1669 |
| 45 | 2040 | 2035 | 2022 | 1997 | 1981 | 1962 |
| 50 | 2341 | 2336 | 2322 | 2294 | 2276 | 2255 |
| 55 | 2669 | 2663 | 2648 | 2617 | 2597 | 2575 |
| 60 | 3025 | 3020 | 3004 | 2972 | 2951 | 2926 |
| 65 | 3398 | 3393 | 3377 | 3343 | 3321 | 3296 |
| 70 | 3785 | 3780 | 3764 | 3730 | 3707 | 3680 |
| 75 | 4177 | 4173 | 4158 | 4122 | 4099 | 4071 |
| 80 | 4561 | 4558 | 4544 | 4510 | 4486 | 4459 |
| 85 | 4933 | 4932 | 4920 | 4888 | 4865 | 4839 |

### Heat of Formation of, and Partial Molal Heat Contents and Free Energies in Phosphoric Acid Solutions

The heat of solution of orthophosphoric acid in water, based on early data, has been summarized[60] and tabulated.[39] Slightly different, but possibly more reliable, values are given in Tables X, XI, XII and XIII for the relative partial molal heat content of phosphoric acid in phosphoric acid solutions, $(\bar{H}_2 - \bar{H}_2^\circ)$, the relative partial molal heat content of water in phosphoric acid solutions, $-(\bar{H}_1 - \bar{H}_1^\circ)$, the relative partial molal free energy of phosphoric acid in phosphoric acid solutions, $(\bar{F}_2 - \bar{F}_2^\circ)$, and the relative partial molal free energy of water in phosphoric acid solutions, $-(\bar{F}_1 - \bar{F}_1^\circ)$, at 15°, 25°, 40°, 60°, 70° and 80°C. for phosphoric acid solutions ranging in concentration from 5% to 85% $H_3PO_4$.[61-3]

*Table XIII.—Relative Partial Molal Free Energy of Water in Orthophosphoric Acid Solutions,* $-(\bar{F}_1 - \bar{F}_1^\circ)$, *g.cal./mole* $H_3PO_4$

| $H_3PO_4$ wt.-% | 15° | 25° | 40° | 60° | 70° | 80° |
|---|---|---|---|---|---|---|
| 5 | 6·15 | 6·46 | 6·98 | 7·79 | 8·25 | 8·76 |
| 10 | 13·62 | 13·79 | 13·99 | 14·14 | 14·10 | 13·98 |
| 15 | 22·18 | 22·66 | 23·36 | 24·22 | 24·58 | 24·92 |
| 20 | 33·15 | 33·62 | 34·18 | 34·66 | 34·79 | 34·86 |
| 25 | 46·57 | 47·44 | 48·72 | 50·49 | 51·45 | 52·47 |
| 30 | 64·22 | 65·14 | 66·49 | 68·40 | 69·45 | 70·53 |
| 35 | 87·35 | 88·21 | 89·41 | 91·02 | 91·87 | 92·72 |
| 40 | 117·9 | 118·8 | 120·0 | 121·4 | 122·2 | 122·9 |
| 45 | 158·0 | 158·8 | 160·0 | 160·8 | 161·2 | 161·6 |
| 50 | 208·7 | 209·3 | 209·8 | 209·9 | 209·7 | 209·4 |
| 55 | 275·2 | 275·6 | 275·7 | 274·8 | 274·0 | 273·0 |
| 60 | 364·4 | 365·2 | 365·7 | 365·2 | 364·6 | 363·9 |
| 65 | 478·1 | 478·7 | 478·6 | 476·8 | 475·4 | 473·7 |
| 70 | 627·7 | 628·5 | 628·4 | 626·4 | 624·7 | 622·6 |
| 75 | 818·3 | 819·4 | 819·6 | 817·5 | 815·5 | 813·0 |
| 80 | 1065 | 1067 | 1068 | 1068 | 1067 | 1065 |
| 85 | 1387 | 1390 | 1393 | 1395 | 1394 | 1393 |

The heats of formation of orthophosphoric acid solutions obtained from the heat contents[62] are shown in Table XIV.

*Table XIV.—Heats of Formation of Orthophosphoric Acid Solutions at* 298·16° K., *kcal./mole* $H_3PO_4$

| $n$H₂O moles | $-\Delta H_f^\circ$ | $n$H₂O moles | $-\Delta H_f^\circ$ |
|---|---|---|---|
| 1 | +305·68 | 100 | 309·16 |
| 2 | 306·64 | 200 | 309·25 |
| 3 | 307·21 | 300 | 309·28 |
| 4 | 307·59 | 400 | 309·30 |
| 5 | 307·84 | 500 | 309·32 |
| 6 | 308·04 | 700 | 309·34 |
| 8 | 308·29 | 1000 | 309·35 |
| 10 | 308·46 | 2000 | 309·38 |
| 12 | 308·57 | 3000 | 309·39 |
| 15 | 308·69 | 4000 | 309·40 |
| 20 | 308·81 | 5000 | 309·40 |
| 25 | 308·88 | 7000 | 309·41 |
| 30 | 308·94 | 10000 | 309·41 |
| 40 | 309·00 | 20000 | 309·42 |
| 50 | 309·05 | 50000 | 309·43 |
| 75 | 309·12 | 100000 | 309·43 |
| | | ∞ | 309·44 |

In order to conform with the heats of formation recently reported[301] for $H_3PO_{4(c)}$ and $H_3PO_{4(l)}$, all the results tabulated above should be increased by 1·18 kcal.

The heats and free energies of formation and entropies of orthophosphoric acid in different reference states at 298·16° K. are as follow:

| | $H_3PO_{4(c)}$ | $H_3PO_{4(l)}$ | $H_3PO_{4(\infty H_2O)}$ |
|---|---|---|---|
| $-\Delta F_f^\circ$ kcal./mole | — | 268·73[39] | 274·40[39] |
| $-\Delta H_f^\circ$ kcal./mole | 306·20[62] | 303·10[62] | 309·44[62] |
| | 305·7 ± 0·3[301] | 302·1 ± 0·3[301] | |
| $S^\circ$, g.-cal./mole°C. | 26·41[2] | 38·3[39] | 37·6[39] |

The heats of neutralization of phosphoric acid to the three stages of ionization (p. 700) are 14·9, 12·3 and 7·5 kcal./mole respectively.[344]

### Specific Heat and Heat of Fusion of Crystalline Orthophosphoric Acid and its Hemihydrate

Although slightly differing heats of fusion based on freezing-point determinations have been reported,[39, 64] the most probable values[2, 301] are as follow:

$$H_3PO_{4(c)} = H_3PO_{4(l)}, \qquad \Delta H^\circ = 3200 \pm 400 \text{ g.-cal./mole}^{301}$$
$$H_3PO_4,\tfrac{1}{2}H_2O_{(c)} = H_3PO_4,\tfrac{1}{2}H_2O_{(l)}, \qquad \Delta H^\circ = 8762 \text{ g.-cal./mole}^{2}$$

The heat capacities, $C_p$, heat content, $(H - H_0^\circ)$, and entropy of the two crystalline forms are contained in Table XV.

*Table XV.—Heat Capacity, Heat Content and Entropy of* $H_3PO_{4(c)}$ *and* $H_3PO_4,\frac{1}{2}H_2O_{(c)}$

| °K | $H_3PO_{4(c)}$ | $H_3PO_4,\frac{1}{2}H_2O_{(c)}$ |
|---|---|---|
| | $C_p$ g.-cal·/°C./mole | |
| 25 | 1·70 | 3·83 |
| 50 | 5·24 | 11·80 |
| 75 | 8·01 | 18·40 |
| 100 | 10·24 | 23·88 |
| 125 | 12·31 | 28·95 |
| 150 | 14·32 | 33·81 |
| 175 | 16·24 | 38·48 |
| 200 | 18·13 | 42·97 |
| 225 | 19·99 | 47·40 |
| 250 | 21·83 | 51·76 |
| 275 | 23·67 | 56·17 |
| 300 | 25·48 | 60·56 |
| 273·16 (0°C.) | 23·53 | 55·84 |
| 298·16 (25°C.) | 25·35 | 60·24 |
| | Heat content $(H - H_0^\circ)$ g.-cal./mole | |
| 273·16 (0°C.) | 3448 | 8118 |
| 298·16 (25°C.) | 4059 | 9569 |
| | Entropy $S^\circ$ g.-cal./°C./mole | |
| 273·16 (0°C.) | 24·27 | 56·65 |
| 298·16 (25°C.) | 26·41 | 61·73 |

### Specific Heat of Aqueous Orthophosphoric Acid Solutions; Partial Molal Heat Capacity

Measurements[65] earlier than those tabulated below were limited to specific heats at 21°C. and average specific heats between this temperature and the boiling points of the acids investigated. Smoothed values from a more detailed and self-consistent set of data[61] are given in Table XVI.

A nomograph presenting these data has been devised.[66]

It has been pointed out that the rapid change in specific heat above 60°C.[61] may be accounted for by changes in the properties of water and the degree of hydration of the orthophosphoric ions present; sulphuric and acetic acids show similar behaviour.

*Table XVI.—Specific Heat $C_p$ of Orthophosphoric Acid Solutions, g.-cal./°C./g.*

| $H_3PO_4$ wt.-% | 15°C. | 25°C. | 40°C. | 60°C. | 70°C. | 80°C. |
|---|---|---|---|---|---|---|
| 0 | 1·0004 | 0·9990 | 0·9987 | 1·0010 | 1·0013 | 1·0030 |
| 10 | 0·9172 | 0·9208 | 0·9251 | 0·9282 | 0·9330 | 0·9347 |
| 20 | 0·8414 | 0·8465 | 0·8534 | 0·8622 | 0·8652 | 0·8639 |
| 30 | 0·7679 | 0·7743 | 0·7833 | 0·7945 | 0·7956 | 0·7968 |
| 40 | 0·6971 | 0·7036 | 0·7134 | 0·7256 | 0·7294 | 0·7342 |
| 50 | 0·6281 | 0·6353 | 0·6477 | 0·6580 | 0·6649 | 0·6674 |
| 60 | 0·5639 | 0·5725 | 0·5838 | 0·5970 | 0·6021 | 0·6042 |
| 70 | 0·5096 | 0·5166 | 0·5264 | 0·5385 | 0·5440 | 0·5474 |
| 80 | 0·4606 | 0·4612 | 0·4746 | 0·4861 | 0·4919 | 0·4941 |
| 90* | 0·4174 | 0·4228 | 0·4294 | 0·4389 | 0·4429 | 0·4454 |
| 100* | 0·3839 | 0·3889 | 0·3918 | 0·4008 | 0·4013 | 0·4010 |

*Extrapolated values

Partial molal heat capacities derived from these data[61] and given in Table XVII, when plotted against concentration, also show abrupt changes in slope at 0·1, 2·2, 4, 8 and 15 $m$ $H_3PO_4$, the break at 2·2 molality being the most pronounced. These, and similar changes with composition in the density, dielectric constant, conductivity, pH and activity at 25°C. possibly correspond to changes in the number or relative concentrations of species in solution.

*Table XVII.—Partial Molal Heat Capacities, $\bar{C}_{p_2}$, g.-cal./°C./mole, of* $H_3PO_4$ *in Orthophosphoric Acid Solution*

| $H_3PO_4$ wt.-% | °C. | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 25 | 40 | 60 | 70 | 80 |
| 10 | 23·95 | 24·84 | 27·20 | 30·09 | 30·24 | 34·48 |
| 20 | 23·30 | 25·05 | 28·02 | 32·64 | 30·60 | 29·05 |
| 30 | 25·94 | 26·80 | 28·02 | 30·77 | 32·18 | 35·43 |
| 40 | 26·92 | 27·62 | 30·45 | 30·58 | 33·00 | 34·69 |
| 50 | 28·46 | 29·87 | 31·32 | 33·29 | 33·99 | 33·14 |
| 60 | 32·06 | 33·10 | 33·70 | 34·93 | 35·10 | 36·35 |
| 70 | 34·85 | 34·94 | 35·52 | 36·27 | 37·09 | 37·40 |
| 80 | 36·07 | 36·46 | 36·97 | 37·74 | 38·26 | 38·41 |
| 90 | 37·13 | 37·61 | 38·01 | 38·84 | 38·97 | 39·09 |
| 100 | 37·63 | 38·11 | 38·39 | 39·28 | 39·33 | 39·33 |

Data for the relative partial molal heat capacity of water in orthophosphoric acid solution, $-(\bar{C}_{p_1} - \bar{C}_{p_1})$, are also available[61]; other partial molal data have been given above (page 674).

## Activity and Degree of Ionization of Orthophosphoric Acid

The activity of orthophosphoric acid at 25°C. has been calculated from vapour pressure measurements of aqueous solutions up to 10 *m*.[35] from e.m.f. measurements using the system[67]: Pb(two-phase amalgam)/$PbHPO_4(s)$, $H_3PO_4(m)/H_2$

$$E^{\circ}_{25} = 0{\cdot}2507 \text{ volt}$$

over the same range of molality, and from the system[68]:

$$Hg/Hg_2HPO_4(s),H_3PO_4(m)/H_2$$
$$E^{\circ}_{25} = -0{\cdot}6359 \text{ volt}$$

over the range 0–4 *m*. The results are compared in Table XVIII.

*Table XVIII.—The Activity, $a_u$ of Orthophosphoric Acid at 25°C.*

| $H_3PO_4$ molality $m$ | $a_u$ | | |
|---|---|---|---|
| | From vapour pressures[34] | From e.m.f. | |
| | | Lead phosphate electrode[67] | Mercurous phosphate electrode[68] |
| 0·02 | 0·01031 | 0·01045 | 0·01154 |
| 0·03 | 0·01738 | 0·01758 | 0·01771 |
| 0·05 | 0·03291 | 0·03331 | 0·0320 |
| 0·08 | 0·05851 | 0·05913 | 0·05521 |
| 0·10 | 0·07688 | 0·07779 | 0·06973 |
| 0·20 | 0·1605 | 0·1708 | 0·1530 |
| 0·30 | 0·2493 | 0·2675 | 0·2386 |
| 0·40 | 0·3417 | 0·3666 | 0·3336 |
| 0·60 | 0·5360 | 0·5809 | 0·5199 |
| 0·80 | 0·7425 | 0·8132 | 0·7211 |
| 1·00 | 0·9615 | 1·06 | 0·9108 |
| 2·00 | 2·275 | 2·585 | 1·965 |
| 4·00 | 6·461 | 7·60 | 4·223 |
| 8·00 | 27·96 | 33·37 | — |
| 10·00 | 49·97 | 58·64 | — |

At concentrations of orthophosphoric acid from 0·02–0·1 *m*., the activities calculated from the vapour pressure measurements are in good agreement with those obtained from the e.m.f. of the lead phosphate electrode; divergence at higher concentrations is attributed to the increased solubility of lead phosphate in the more concentrated acid.

The values reported by Larson[68] do not depend on the applicability of the Debye–Hückel limiting law at concentrations in the range 0–0·1 *m*., as do those of Elmore *et al.*[35] and Mason and Blum[67]; nor, in the absence of data, have any corrections been made for the solubility of mercurous phosphate.

The activity coefficient of the undissociated part of the orthophosphoric acid, ($\gamma_u \equiv 1$), does not vary over the range 0·02–0·1 *m*.

The activity of water in solutions of orthophosphoric acid, as calculated from the vapour pressure of the solutions,[35] is shown in Table XIX. These values are generally in good agreement with previous data.[30, 34]

The degree of ionization of orthophosphoric acid has been calculated[35] from conductance data[69] and ionization constants[70] by the method of Banks,[71] giving the values in Table XX, which were used to calculate some of the activities listed in Table XIX.

## The Acidity Function of Orthophosphoric Acid

The acidity function, $H_0$, which measures the ability of a medium to transfer a proton to a neutral molecule, is defined by Hammett[72] as:

$$-H_0 = \log a_{\mathrm{H}^+} + \log \frac{f_{\mathrm{B}}}{f_{\mathrm{BH}^+}},$$

where $a_{\mathrm{H}^+}$ is the hydrogen ion activity and $f_{\mathrm{B}}$ and $f_{\mathrm{BH}^+}$ are the activity coefficients of the neutral molecule and conjugate acid respectively; in dilute solution the acidity function is substantially the same as the pH.

*Table XIX.—Activity of Water ($a_1$) in Orthophosphoric Acid Solutions, at 25°C.*

| $H_3PO_4$ molality $m$ | Activity of water ($a_1$) | Reference standard |
|---|---|---|
| 0·1659 | 0·9964 | NaCl, KCl solution |
| 0·3321 | 0·9932 | ,, |
| 0·5899 | 0·9881 | ,, |
| 1·0134 | 0·9796 | ,, |
| 2·0445 | 0·9570 | ,, |
| 5·7063 | 0·8552 | ,, |
| 10·284 | 0·6990 | Sulphuric acid |
| 20·708 | 0·4084 | ,, |
| 50·010 | 0·1202 | ,, |
| 74·26 | 0·0627 | ,, |

*Table XX.—The Degree of Ionization of Orthophosphoric Acid Solutions, at 25°C.*

| $H_3PO_4$ molality $m$ | Degree of ionization $\alpha$ |
|---|---|
| 0·01 | 0·6027 |
| 0·02 | 0·4946 |
| 0·03 | 0·4359 |
| 0·04 | 0·3970 |
| 0·05 | 0·3688 |
| 0·06 | 0·3473 |
| 0·07 | 0·3301 |
| 0·08 | 0·3162 |
| 0·09 | 0·3040 |
| 0·10 | 0·2938 |

The first measurements on orthophosphoric acid,[73] using the method of Hammett and Deyrup,[72] gave values for $H_0$ varying from $+1{\cdot}08$ to $-3{\cdot}34$ for acid solutions ranging from 5 to 80% $H_3PO_4$, at 19 ± 2·0°C. These data were extended, by similar methods, to cover solutions containing 62–86% of $P_2O_5$, that is, to include pyrophosphoric and other polyphosphoric acids.[74-5]

The last data[74-5] are in good agreement below 62% $P_2O_5$ (86% $H_3PO_4$), but contrary to Gel'bshtein *et al.*[74] the results of Downing and Pearson do not show a maximum in the plot of $H_0$ versus % $P_2O_5$ at 80% $P_2O_5$, corresponding approximately with the formula $H_4P_2O_7$ for pyrophosphoric acid. As other parameters such as density, viscosity, refractive index and composition show regular change over the concentration range in question, it is now believed that the reported maximum for $H_0$ can be ascribed to decomposition of the particular indicator used to measure this quantity, and not to an abrupt change in the nature of the acid, especially since later work by the same authors did not show any maximum value for $H_0$.[345] According to Downing and Pearson the value of $H_0$, at 25°C., changes steadily from $-4{\cdot}1$ for 89·6% $H_3PO_4$ (65% $P_2O_5$) to $-7{\cdot}1$ for 118% $H_3PO_4$ (85·7% $P_2O_5$). Gel'bshtein *et al.* now confirm this monotonic variation over a wider range of concentration, from $+0{\cdot}92$ for 3·6% $H_3PO_4$ (5% $P_2O_5$), through $-4{\cdot}03$ at 65% $P_2O_5$ to $-6{\cdot}84$ at 85% $P_2O_5$.[345]

The acidity function can also be correlated with the activities of water and phosphoric acid in aqueous solutions by the linear relationship[76]:

$$H_0 = -0{\cdot}80+0{\cdot}98 \log \frac{(a_{HX})}{a_{H_2O}}$$

which fits the data for $H_0$[73] and activities.[35] Hydrochloric and perchloric acids behave similarly, but sulphuric acid shows a curvilinear relationship. On any basis of comparison the acidities of the conventional strong acids are considerably higher than that of orthophosphoric acid.

The acidity function of orthophosphoric acid in acetic acid has also been studied.[77-8]

## Refractive Index of Orthophosphoric Acid

Systematic studies of the refractive index of orthophosphoric acids have not been reported; values quoted in Table XXI[79] cover the more dilute range of concentrations and the linear equation:

$$\%\ P_2O_5 = 522{\cdot}09\ n_D^{25} - 685{\cdot}07$$

has been proposed[75] for solutions containing 60–85% of $P_2O_5$. Over a wider concentration range the refractive index, $n$, of phosphoric acid solutions at 25°C. for the Hg (green) line at 5460·7 A. is said to be given by the equation:

$$n = 1{\cdot}333977+0{\cdot}001999w^{1/2}+0{\cdot}07155w+0{\cdot}0868841w^{3/2} -0{\cdot}2375104w^2+0{\cdot}3625678w^{5/2}-0{\cdot}1669960w^3$$

where $w$ is the concentration, weight fraction, of $H_3PO_4$ from 0 to 0·90.[346]

*Table XXI.—Refractive Index, $n_D^{17{\cdot}5}$, of Orthophosphoric Acid Solutions*

| % $H_3PO_4$ | % $P_2O_5$ | $n_D^{17{\cdot}5}$ |
|---|---|---|
| 0 | 0 | 1·33320 |
| 5 | 3·62 | 1·33775 |
| 10 | 7·24 | 1·34203 |
| 20 | 14·49 | 1·35032 |
| 30 | 21·73 | 1·35846 |

The two sets[75,79] of data do not fit on extrapolation, nor are earlier values[80] in agreement with those quoted in Table XXI, partly owing to the determinations having been made at different temperatures.

Differential refractometry has been employed to study the degree of dissociation of dilute solutions of orthophosphoric acid[81] and a value of $n_D^{20}=1{\cdot}4503$ has been reported for anhydrous orthophosphoric acid crystals.[4]

## Magnetic Susceptibility and Dielectric Constant of Orthophosphoric Acid

The molar magnetic susceptibility, $-\chi_m$, of orthophosphoric acid has been measured[82-3] and is of the order of $45\times10^{-6}$.

The variation with concentration of the dielectric constant of dilute aqueous solutions of phosphoric acid has been investigated. A point of inflection in the curve plotting dielectric constant against concentration can be attributed to hydration of the ions; some average values[84] for solutions at 20·2° to 21·5°C. are contained in Table XXII.

*Table XXII.—Dielectric Constant of Orthophosphoric Acid Solutions*

| $H_3PO_4$ wt.-% | Dielectric constant $\epsilon$ |
|---|---|
| 0 | 80·0 |
| 0·10 | 77·5 |
| 0·15 | 74·9 |
| 0·20 | 68·4 |
| 0·25 | 73·7 |
| 0·30 | 79·0 |
| 0·40 | 80·6 |
| 0·50 | 80·4 |

Values at higher concentrations have also been recorded. The dielectric constant of 100% $H_3PO_4$ at 25°C. and 4·89–19·32 Mc/sec. is $61 \pm 12$, the high value confirming association by hydrogen bonding[347] (see p. 571). The static dielectric constant, $\epsilon_0$, at 3, 10 and 17 Gc/sec. decreases from 78 for water to a minimum of 19 for 65 *m* $H_3PO_4$,[348] confirming previous observations at lower frequencies.[347]

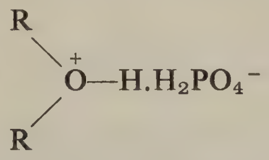
## Solubility of Orthophosphoric Acid in Organic Solvents

Orthophosphoric acid is soluble in a large number of organic solvents.

Thermal analysis of the system diethyl ether–orthophosphoric acid in the concentration range 0–17·5% ether showed[85] the existence of two compounds:

| | | |
|---|---|---|
| | $(C_2H_5)_2O,6H_3PO_4$ | m.p. 28·2°C. |
| and | $(C_2H_5)_2O,4H_3PO_4$ | m.p. 30·0°C. |

An equimolecular compound, $(C_2H_5)_2O,H_3PO_4$, reported from calorimetric measurements,[86] is believed to have an oxonium type structure:



but the compound has not been isolated in the solid state.

The partition coefficient at 23°C. for $H_3PO_4$ between water and diethyl ether[87] is shown in Table XXIII.

*Table XXIII.—Partition Coefficient of* $H_3PO_4$ *between Water and Diethyl Ether at* 23°C.

| g. $H_3PO_4$ in | | Partition coefficient |
|---|---|---|
| 100 g. $H_2O$ | 100 g. $(C_2H_5)_2O$ | |
| 34·8 | 0·01 | 0·00064 |
| 82·0 | 0·26 | 0·0032 |
| 105·0 | 0·95 | 0·009 |
| 136·5 | 1·78 | 0·136 |

The solubility of diethyl ether in orthophosphoric acid is small.[88]

The application in industrial practice of the solubility of orthophosphoric acid in organic compounds to solvent extraction processes for the separation and purification of the acid has been mentioned (Section XXIV, page 667), and has resulted in a search for the most effective solvents. Of eighteen investigated the best were found to be *iso*amyl alcohol and fusel oil[89]; in a more recent investigation[90] the most effective solvents out of the twenty-four mentioned were tertiary amyl alcohol, butanol, *cyclo*hexanol, 2-hydroxyethyl-*n*-hexyl ether, *cyclo*pentanone and tri-*n*-butyl phosphate. The distribution coefficients, $K = C_0/C_w$, where $C_0$ is the equilibrium concentration of total solute in the organic phase, in g. moles/l. and $C_w$ that of the total solute in the aqueous phase in the same units for all the solvents, are given in Table XXIV.

*Table XXIV.—Distribution Coefficients, K, at* 25°C., *for* $H_3PO_4$ *between Water and Various Solvents*

| Solvent | *K* |
|---|---|
| *tert*-amyl alcohol | 0·1648 |
| *n*-butanol | 0·1462 |
| *cyclo*hexanol | 0·0908 |
| 2-hydroxyethyl-*n*-hexyl ether | 0·1294 |
| octylene glycol | 0·0674 |
| *cyclo*pentanone | 0·2371 |
| *iso*amyl alcohol | 0·0471 |
| *n*-amyl alcohol | 0·0478 |
| 2-hydroxyethyl phenyl ether | 0·0437 |
| *n*-hexyl alcohol | 0·0312 |
| benzyl alcohol | 0·0264 |
| tri-*n*-butyl phosphate | 0·1149 |
| 2-ethyl-l-butanol | 0·0149 |
| *o*-chlorophenol | 0·0050 |
| *n*-butyl ether | 0·00003 |
| triperfluorobutylamine | 0·0000 |
| acetophenone | 0·0005 |
| ethyleneglycol dibutyl ether | 0·0000 |
| thiophen | 0·0000 |
| methyl *iso*butyl ketone | 0·0003 |
| chloroform | 0·00007 |
| carbon tetrachloride | 0·00007 |
| *n*-hexyl ether | 0·0034 |
| 1-pentamethiol | 0·0004 |

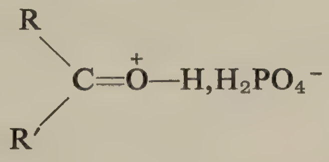
The theory of the extraction by such solvents of orthophosphoric acid alone, or in admixture with hydrochloric acid, and the effects on the distribution coefficient of such factors as the chemical and physical character of the solvent, acid concentration, acidity, and activity coefficients have been discussed on the basis of data obtained in such studies.[90, 304–6] A similar study of the effect of electrolytes on the distribution of orthophosphoric acid between water and *iso*amyl alcohol showed, as expected, that the proportion of acid dissolving in the organic phase increased with increasing salt concentration. The effectiveness of a series of chlorides in altering the distribution coefficient was related to the charge and radius of the cations:

$$Mg^{++} > Li^{+} > Ca^{++} > Sr^{++} > Na^{+} > NH_4^{+} > K^{+}$$ [307]

Orthophosphoric acid hemihydrate dissolves readily in benzyl cyanide to the extent of 0·5 g. $H_3PO_4,\frac{1}{2}H_2O$ per ml., and if dioxan is then added, the addition compound dioxan, $2H_3PO_4$, m.p. 82°–85°C., crystallizes out.[91] The anhydrous acid is soluble to the extent of 26% in ethyl acetate, in which solution *trans*-esterification is thought, from Raman spectroscopic evidence,[22] to occur to a slight extent.

The solubilities of phenol and of citric, malic, oxalic, succinic and *iso*valeric acids in orthophosphoric acid of various concentrations have been measured[92] and there are indications that compound formation, similar to that mentioned for diethyl ether, takes place.

Freezing studies[93] on a wide range of organic substances, including acids, esters, aldehydes, ketones, phenols and acid anhydrides, with orthophosphoric acid as one component, showed that several addition compounds could be isolated from the system as crystalline compounds, their general formula being of the type:



The compounds which formed such oxonium salts were acetic and pyruvic acids, benzaldehyde, anisaldehyde, acetophenone, benzophenone and coumarin. Sulphuric acid forms such compounds more readily than orthophosphoric acid, by virtue of its higher acidity function (q.v.).

The interaction between phosphoric acid and polar organic solvents has also been studied by proton magnetic resonance. The solvents were of two types:

I (including $Me_2SO$, $Me_2CO$, $(MeO)_3PO$ and $Et_2O$); polar solvents which form complexes, and also dissociate and eventually ionize the acid, the solvent donor properties decreasing in the order shown above.

II (including MeOH, EtOH (and $H_2O$)); polar solvents which are themselves associated, and besides exhibiting the above behaviour, also dissociate themselves and exchange protons with phosphoric acid.[349]

The infra-red spectra of non-aqueous solutions of phosphoric and deuterophosphoric acid have been recorded.[350]

The ternary system orthophosphoric acid–phenol–water[94] is of interest because it exhibits closed layering isotherms in the temperature range 68°–100°C., which are the upper binary critical temperature for the system phenol–water and the lower binary critical temperature for the system orthophosphoric acid–phenol, respectively; closed isotherms are typical when such conditions occur. The compound $H_3PO_4,\frac{1}{2}H_2O$ was noted in the relevant binary system.

Fewer data are available for the solubility of orthophosphoric acid in inorganic solvents other than water. It is, however, known to be sparingly soluble in anhydrous liquid hydrogen chloride, and does not act as a solvo-acid in this medium.[308]

The solubility of oxygen and paraffin hydrocarbons in phosphoric acid solutions has been measured in connection with research on fuel cells.[351-3] The solubility of oxygen at 25° and 30°C., as determined by a gas-liquid chromatographic method,[352] falls off rapidly and continuously with increasing acid concentration.[351] A correlation has been presented to enable the solubility of oxygen and hydrocarbons in 85–105% phosphoric acid to be predicted with reasonable accuracy.[353]

## Electrical and Thermal Conductivity of Orthophosphoric Acid

### SPECIFIC AND EQUIVALENT CONDUCTIVITY

Table XXV[39] contains information derived from sources prior to 1927, together with more recent data[95] obtained at 25°C.

Measurements have also been reported[50] for slightly higher concentrations of acid than those of Noyes *et al.*,[96] but not over as wide a range of temperature. At 25°C. they are only in agreement with the values given in Table XXV at concentrations below 30% and above 80% $H_3PO_4$; inside this range they are about 10–15% lower.

At 50°C. they are also much lower than numerous values quoted at the same temperature[8]; the data at 0° and 25°C. are in excellent agreement with those given in Table XXV. Values at 50°C. are therefore given from reference 8 in Table XXVI.

*Table XXV.—Electrical Conductivity of Aqueous Orthophosphoric Acid*

| $H_3PO_4$ wt.-% | Specific ($K$) and equivalent ($\Omega$) conductivities at | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 0°C. | | 18°C. | | 25°C. | | 29·3°C. | |
| | $K$ | $\Omega$ | $K$ | $\Omega$ | $K$ | $\Omega$ | $K$ | $\Omega$ |
| 0 | — | — | — | — | — | 126·1 | — | 132 |
| 1 | — | — | — | — | 0·0102 | 33·3 | — | — |
| 2 | — | — | — | — | 0·0175 | 28·3 | — | — |
| 3 | — | — | — | — | 0·0226 | 24·3 | — | — |
| 4 | — | — | — | — | 0·0281 | 22·5 | — | — |
| 5 | 0·0409 | 26·1 | — | — | 0·0334 | 21·3 | — | — |
| 10 | 0·0615 | 19·1 | 0·0566 | 17·6 | 0·0617 | 19·2 | — | — |
| 15 | 0·0772 | 15·5 | 0·0850 | 17·1 | 0·0918 | 18·5 | — | — |
| 20 | 0·0934 | 13·7 | 0·1129 | 16·6 | 0·1236 | 18·2 | — | — |
| 25 | 0·1096 | 12·5 | 0·1402 | 16·0 | 0·1553 | 17·7 | — | — |
| 30 | 0·1259 | 11·6 | 0·1654 | 15·3 | 0·1836 | 17·0 | — | — |
| 35 | 0·1415 | 10·9 | 0·1858 | 14·3 | 0·2068 | 15·9 | — | — |
| 40 | 0·1472 | 9·6 | 0·2010 | 13·1 | 0·2236 | 14·6 | — | — |
| 45 | 0·1488 | 8·37 | 0·2087 | 11·7 | 0·2336 | 13·6 | — | — |
| 50 | 0·1427 | 7·00 | 0·2073 | 10·2 | 0·2324 | 11·4 | — | — |
| 55 | 0·1317 | 5·68 | 0·1978 | 8·53 | 0·2263 | 9·77 | — | — |
| 60 | 0·1195 | 4·57 | 0·1833 | 7·00 | 0·2117 | 8·10 | — | — |
| 65 | 0·1052 | 3·59 | 0·1650 | 5·63 | 0·1905 | 6·50 | — | — |
| 70 | 0·0844 | 2·59 | 0·1436 | 4·40 | 0·1656 | 5·07 | — | — |
| 75 | 0·0608 | 1·84 | 0·1209 | 3·65 | 0·1373 | 3·80 | — | — |
| 80 | 0·0460 | 1·15 | 0·0979 | 2·46 | 0·1118 | 2·80 | — | — |
| 85 | 0·0348 | 0·79 | 0·0780 | 1·78 | 0·0907 | 2·07 | — | — |
| 90 | 0·0254 | 0·53 | — | — | 0·0673 | 1·40 | 0·0850 | 1·77 |
| 95 | 0·0184 | 0·35 | — | — | 0·0612 | 1·17 | 0·0696 | 1·33 |

$K$=specific conductance, ohm$^{-1}$ cm.$^{-1}$

$\Omega = KV$=equivalent conductivity, ohm$^{-1}$ cm.$^2$, where $V$=volume of solution (ml.) containing 1 g. equivalent of $H_3PO_4$.

*Table XXVI.—Electrical Conductivity, K ohm$^{-1}$ cm.$^{-1}$, of Aqueous Orthophosphoric Acid at 50°C.*

| $H_3PO_4$ wt.-% | $K$ ohm$^{-1}$ cm.$^{-1}$ | $H_3PO_4$ wt.-% | $K$ ohm$^{-1}$ cm.$^{-1}$ |
| --- | --- | --- | --- |
| 0·382 | 0·0062 | 64·46 | 0·2856 |
| 2·30 | 0·0226 | 68·89 | 0·2617 |
| 3·77 | 0·0311 | 71·60 | 0·2462 |
| 9·32 | 0·0679 | 75·53 | 0·2214 |
| 15·64 | 0·1135 | 81·32 | 0·1913 |
| 25·04 | 0·1882 | 82·72 | 0·1818 |
| 38·91 | 0·2841 | 83·58 | 0·1794 |
| 42·78 | 0·3010 | 88·50 | 0·1509 |
| 44·94 | 0·3091 | 89·38 | 0·1470 |
| 45·54 | 0·3098 | 90·82 | 0·1413 |
| 47·40 | 0·3134 | 92·24 | 0·1364 |
| 48·00 | 0·3142 | 93·74 | 0·1319 |
| 51·83 | 0·3171 | 95·69 | 0·1221 |
| 55·25 | 0·3137 | 96·40 | 0·1181 |
| 59·71 | 0·3016 | 98·30 | 0·1090 |
| 62·32 | 0·2937 | 98·50 | 0·1072 |

Maxima in the specific conductance–concentration curves in the region of 40–50% $H_3PO_4$, tending to higher concentrations with increasing temperature,[95, 50, 8] agree with previous reports[96] and suggest the presence of hydrated ions. However, conductivity isotherms corrected for variation of viscosity and molar volume are claimed to show no such maximum.[309]

According to most authors, the temperature coefficient of specific conductivity changes from positive to negative as the temperature increases and the temperature of maximum conductivity varies with the acid concentration[8] as shown in Fig. 3.

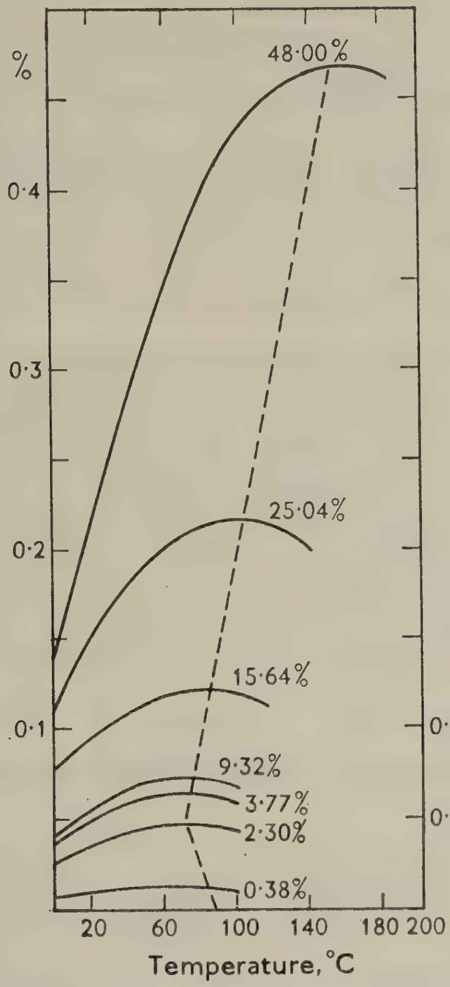


FIG. 3.—Variation of specific conductivity of orthophosphoric acid with temperature

More recent studies of the conductivity of a series of acids of more than 90% $H_3PO_4$ content show that in this case also conductivity increases with temperature over the range 20° to 200°C. At any particular temperature the conductivity falls with increasing $P_2O_5$ concentration.[310, 354] Values for the equivalent conductivity of more dilute (0·01–1·5 N.) phosphoric acid have been recorded as high as 300°C.[355]

A single set of observations on 0·13 M. (1·08% $H_3PO_4$) orthophosphoric acid, at temperatures up to 200°C. and pressures up to 15·30 atm. also shows a maximum in specific conductivity at about 70°C.[97]

The surprisingly low limiting equivalent conductance of the dihydrogen phosphate ion ($\lambda^{\circ}_{H_2PO_4^-}$), reported as $33 \pm 1{\cdot}0$ ohm$^{-1}$ cm.$^2$ on the basis of calculations from the e.m.f. of suitable concentration cells using the lead amalgam–lead hydrogen phosphate electrode,[98] was in agreement with values derived from the conductances of $KH_2PO_4$ and $Na_2HPO_4$.[95] The validity of the interpretation of these data was, however, questioned,[98] and recalculation gave an even lower value ($\lambda^{\circ}_{H_2PO_4^-} = 16$ ohm$^{-1}$ cm.$^2$) which was apparently confirmed by some fresh measurements of e.m.f.

and transference numbers, using concentration cells with a mercury–dimercury hydrogen phosphate electrode system. However, a further determination of the transference number of $H_3PO_4$ by the moving boundary method gave quite different results, which cast doubt upon the accuracy of the e.m.f. method in regions of low concentration. These new data led to a value of $\lambda^\circ_A = 40{\cdot}2$ ohm$^{-1}$ cm.$^{-2}$ for the limiting conductance of the [$H_2PO_4^-$] ion.[356] Nevertheless they suggested that the cationic transference number $t_H$ increases with increasing concentration, an observation which was not supported by other workers.[98, 357, 359] A later study[357] by a similar method showed that these data could all be reconciled by assuming the occurrence of hydrogen bonded triple ions, $H_2PO_4^-.H^+.H_2PO_4^-$ with a formation constant of 3 l./mole. Recalculation of the data of[356], allowing for triple ion formation and for hydrolysis in the following $KH_2PO_4$ solution, gave a value of $\lambda^\circ_A = 35{\cdot}6$ ohm$^{-1}$ cm.$^2$. This was in better agreement with subsequent values of 31·9,[368], 32·3[357] and 32·8 ([357] recalc. from the data of[95]) ohm$^{-1}$ cm.$^2$ In order to account for the difference in the values of $\lambda^\circ_{H_2PO_4^-}$ derived from conductance and e.m.f. data, the presence, even in dilute solutions, of the species $H_4PO_4^+$ had been suggested[98, 303] according to the equilibrium:

$$H^+ + H_3PO_4 \rightleftharpoons H_4PO_4^+$$

and if this were so calculation would lead to the value of 250 ohm$^{-1}$ cm.$^2$ for $\lambda^\circ_{H_4PO_4^+}$. Some support for this view has been derived from a study of the exchange of oxygen between phosphoric acid and water as a function of concentration and temperature (155°–170°C.) The exchange velocity fell to a minimum value at an acid concentration of 2–2·5 M. The results suggest the presence of $H_4PO_4^+$ in concentrated solutions, while in dilute solutions $H_2PO_4^-$ is probably the active exchange agent.[358] However, in view of the close correlation between results from the conductance and moving boundary methods, it is more likely that the discrepancy shown by the e.m.f. method is due to the fact that the method of calculation magnifies any errors in the e.m.f. data, particularly at low concentrations.[356-7]

### TRANSFERENCE NUMBER

The transference numbers ($t_H$) for orthophosphoric acid, at 25°C.,[98] are contained in Table XXVII.

*Table XXVII.—Transference Numbers for Orthophosphoric Acid Solutions at* 25°C.

| Molarity | 0·02 | 0·10 | 0·50 | 2·00 | 4·00 |
|---|---|---|---|---|---|
| $t_H$ | 0·952 | 0·933 | 0·914 | 0·897 | 0·889 |

Transference numbers of the phosphate ($H_2PO_4^-$) anion have been determined at 25°C by a radioactive ($^{32}P$) modification of the Hittorf method. The range of concentration covered (0·027–0·43 mol. fraction) was much greater than in previous work (e.g. Ref. 98). The isotherm shows a maximum value of 0·065 g. mole F$^{-1}$ at an acid mol. fraction of 0·15.[359]

### CONDUCTIVITY IN MELTS

The mechanism of electrical conduction in melts of anhydrous[4] and hemihydrated[5] orthophosphoric acid has been studied and provides some evidence in support of the $H_4PO_4^+$ anion mentioned previously and also of the presence of pyrophosphoric acid in liquid anhydrous orthophosphoric acid. The abnormally high electrical conductivity of the latter (similar in this respect to sulphuric acid[99]) is believed to be due to the $H_2PO_4^-$ ion conducting current by a proton-switch mechanism[4, 22, 343, 359] (see also Ref. 360). The ionic equilibrium may be represented as follows:

$$(a) \qquad 2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^-$$

However, the electrical conductivity of fused orthophosphoric acid falls slowly with time to an equilibrium value corresponding to the formation of pyrophosphoric acid, thus:

$$(b) \qquad 2H_3PO_4 \rightleftharpoons H_3O^+ + H_3P_2O_7^-$$

for the existence of which, in such a melt, there is abundant evidence from chromatographic analysis,[100-1] cryoscopic and e.m.f. measurements[361] and isotope exchange studies.[102] The observed 15% decrease in conductivity corresponds to 7·5 mole-% of pyrophosphoric acid.

If pure crystalline orthophosphoric acid, m.p. 42·35°C., is kept molten for several weeks, its freezing point falls to 34·6°C., owing to the setting up of the equilibrium represented by equation (*b*); cryoscopic calculations from this freezing-point depression lead to 5·8 mole-% of pyrophosphoric acid,[4] in fair agreement with the values deduced from conductivity decrease, chromatography (6·5 mole-%) and isotopic exchange studies.[102]

Measurements of the conductivity of orthophosphoric and trideuterophosphoric acids made quickly after melting and given in Table XXVIII,[4] are thought to be preferable to earlier values, on account of the slow change referred to above.

*Table XXVIII.—Specific Conductance (K) of Orthophosphoric and Trideuterophosphoric Acid, ohm$^{-1}$ cm.$^{-1}$ × 10$^2$*

| Temperature °C. | 25 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| $H_3PO_4$ | 4·675 | 5·589 | 7·680 | 10·13 | 12·70 |
| $D_3PO_4$ | 2·818 | 3·378 | 4·632 | 5·94 | 7·261 |

Thus deuteration lowers the specific conductivity of orthophosphoric acid by about 60%. Later data covering a wider range of concentrations (62–86% $P_2O_5$)[362] are in reasonable agreement with the values of Greenwood and Thompson[4] but differ slightly from the values of previous authors.[310, 363]

According to the recent measurements of Greenwood and Thompson,[4] although there is a change in the slope of the 40°C. isotherm of the composition–conductivity diagram (see Fig. 4), there is no minimum and neither is there an inflection in the region of composition corresponding to the hemihydrate $2H_3PO_4,H_2O$. The change of slope occurs at 25 mole-% of $P_2O_5$, that is to say at a composition corresponding to $H_3PO_4$. Addition of water to an acid of this composition increases and addition of phosphoric oxide decreases the conductivity. It is suggested[4] that, being a more powerful proton-acceptor than $H_3PO_4$, water removed protons from $H_4PO_4^+$ and thus raises the concentration of the current-carrying $H_2PO_4^-$ ion, as follows:

$$(c) \qquad 2H_4PO_4^+ + 2H_2O \rightarrow 2H_3O^+ + 2H_3PO_4$$

$$(d) \qquad 2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^-$$

the overall effect being:

$$(e) \qquad H_4PO_4^+ + 2H_2O \rightarrow 2H_3O^+ + H_2PO_4^-$$

By analogy with the sulphuric acid system,[103] the hydroxonium ion is unlikely to have abnormal mobility and the increase in conductivity may therefore be ascribed to the increased concentration of the $H_2PO_4^-$ ion. On the other hand, addition of phosphoric oxide, which reduces conductivity, involves the more complex solvolysis of the $P_4O_{10}$ molecule (q.v.), but the overall reaction can probably be written:

$$(f) \qquad P_4O_{10} + 8H_3PO_4 \rightarrow 6H_4P_2O_7$$

with some dissociation of the pyrophosphoric acid by the equilibrium:

$$(g) \qquad H_4P_2O_7 + H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_3P_2O_7^-$$

As conductivity decreases sharply, and neither of these ions is thought to have appreciable abnormal mobility, the fall is due to the decrease in $H_2PO_4^-$ ion concentration by the removal of orthophosphoric acid (equations (*f*) and (*g*)). The lack of mobility of $H_3P_2O_7^-$ probably resembles that of the $HS_2O_7^-$ ion in sulphuric acid.[104] $H_4PO_4^+$ lacks a dipole moment, and hence any proton-switches in which it was involved would be randomly effected and not in the preferred direction of the applied field.

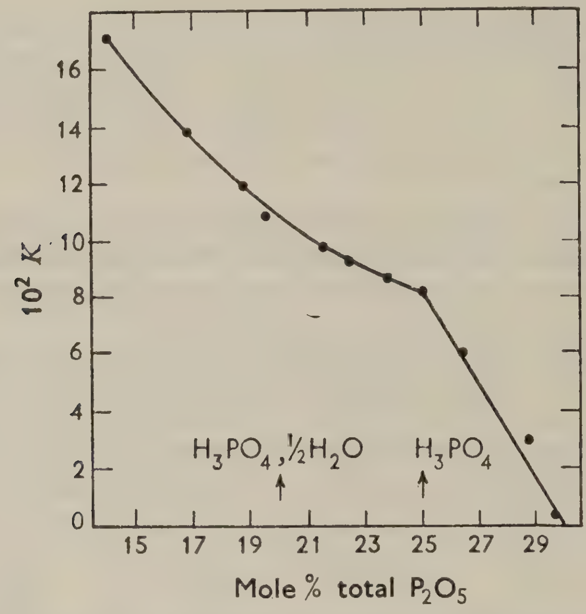


FIG. 4—Conductivity–composition isotherm for $H_2O$–$P_2O_5$ at 40°C.

The extent of the protolysis described by equation (*a*) has been estimated[4] and is compared with that for sulphuric acid and water:

$$K_{(\text{apparent})}[H_4PO_4^+][H_2PO_4^-] = 1{\cdot}7 \times 10^{-2} \text{ mole}^2 \text{ kg.}^{-2} \text{ at } 25°\text{C.}$$
$$(H_2SO_4) = 2{\cdot}9 \times 10^{-4} \text{ mole}^2 \text{ kg.}^{-2} \text{ at } 25°\text{C.}$$
$$(H_2O) = 1{\cdot}01 \times 10^{-14} \text{ mole}^2 \text{ kg.}^{-2} \text{ at } 25°\text{C.}$$

The initial concentration of ions in molten orthophosphoric acid is therefore about eight times that in sulphuric acid and stronger by a factor of $10^6$ compared with water.

Although no discontinuity was observed in the conductivity–mole % $P_2O_5$ curve, shown in Fig. 4, at the composition $2H_3PO_4,H_2O$ the hemihydrate certainly exists as a solid phase; its high electrical conductivity in the molten state is almost double that of the freshly molten anhydrous acid, and has also been shown by transport measurements to be due to the presence of the anomalously conducting species, $H_2PO_4^-$, which provides a proton-switch mechanism. Unlike the anhydrous acid, however, the conductivity of fresh melts of the hemihydrate does not vary with time.[5]

*Table XXIX.—Specific Conductance (K) of Molten Orthophosphoric Acid Hemihydrate, ohm$^{-1}$ cm.$^{-1}$ × $10^2$*

| °C. | 25 | 30 | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|---|
| $2H_3PO_4,H_2O$ (melt) | 7·008 | 8·230 | 10·99 | 14·66 | 17·50 | 21·21 |

The conductivity of the solid hemihydrate is much less than that of a liquid with the same composition, Table XXX.

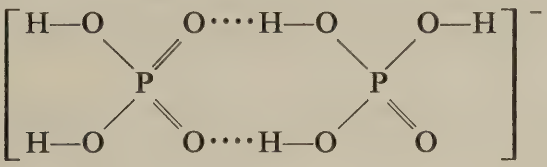
*Table XXX.—Specific Conductance (K) of Crystalline Orthophosphoric Acid Hemihydrate, ohm$^{-1}$ cm.$^{-1}$ × 10$^3$*

| °C. | 19 | 21 | 23 | 25 | 26 |
|---|---|---|---|---|---|
| $2H_3PO_4,H_2O$ (cryst.) | 0·97 | 1·22 | 1·63 | 2·36 | 3·12 |

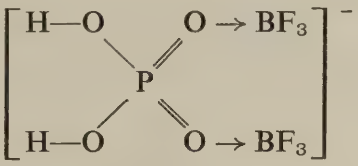
It has been suggested[5] that, when molten hemihydrate ionizes, the anomalously conducting ion $H_2PO_4^-$ solvates with the liberated phosphoric acid thus:

$$(h) \qquad 2H_3PO_4 + H_2O \rightarrow 2H_3PO_4,H_2O \rightleftharpoons H_3O^+ + H_3PO_4,H_2PO_4^-$$

and that the stability of the solvated ion arises from hydrogen-bonding, for example,

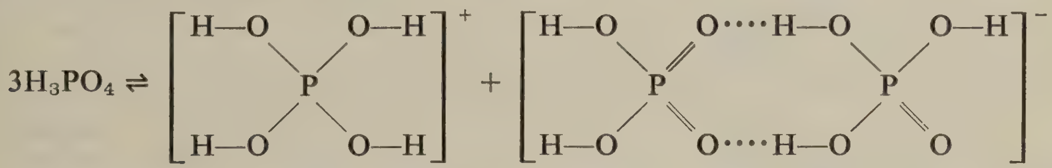


It is of interest, in this connection, to note that in the absence of hydrogen bridges in the postulated structure for the boron trifluoride ion-complex of orthophosphoric acid:



the proton-switch conduction mechanism is suppressed.[105] It is also possible that the $H_2PO_4^-$ ion is solvated in melts of anhydrous orthophosphoric acid, for example,

(*i*)



On the basis of equation (*h*), the autoprotolysis constant of phosphoric acid hemihydrate at 25°C. has been calculated, and is slightly larger than that of the parent acid:

$$K_{(\text{apparent})}(2H_3PO_4,H_2O) \simeq 4{\cdot}4 \times 10^{-2} \text{ mole}^2 \text{ kg.}^{-2}$$

### CONDUCTIVITY OF AQUEOUS $H_3PO_4$–HCl AND $H_3PO_4$–$N_2O_4$

The abnormally low electrical conductivities reported by Pessel[106] for mixtures of orthophosphoric acid and hydrochloric acid were later[107] attributed to the unrecognized presence of sodium salts in the original preparations; mixtures of pure orthophosphoric acid, prepared from phosphoric oxide, with hydrochloric acid or sulphuric acid had conductivities of the orders expected. However the conductimetric and cryoscopic behaviour of the $H_3PO_4$–$H_2SO_4$ and similar systems has been explained by assuming association[343, 369]:

$$2H_3PO_4 + H_2SO_4 \rightarrow [P(OH)_4{}^+]_2SO_4{}^{--}$$

while infra-red[328] and conductivity-transference number[365] studies suggested the existence of the species $2H_2SO_4,H_3PO_4$ in a mixture containing 0·31 mole fraction of $H_3PO_4$.

The effect on the electrical conductivity of replacing water in hydrochloric acid by orthophosphoric acid has been systematically studied. For solutions of hydrochloric acid less than 1N. the conductivity increases with added orthophosphoric acid, but for solutions of higher normality the reverse is true. These changes have been discussed in terms of ion concentration and viscosity.[108]

Solutions of dinitrogen tetroxide, $N_2O_4$, in orthophosphoric acid also exhibit a maximum in their conductivity–concentration curves,[109] at 0·06 mole-% of $N_2O_4$, which is thought to be connected with a change in colour from colourless to yellow. Similar effects have been noted for nitryl fluoride, $NO_2F$.[110] Solutions containing more than 1 mole-% $NO_2F$ are coloured and at 60 mole-% a solid separates. The conductivity–concentration curve passes through a small initial maximum at the lower and through a second blunt maximum at the higher concentration; all these phenomena are indicative of complex formation.

### THERMAL CONDUCTIVITY

Few data are available on the thermal conductivity of phosphoric acid, but a nomograph covering the range 5–50% has been constructed[311] (Fig. 5).

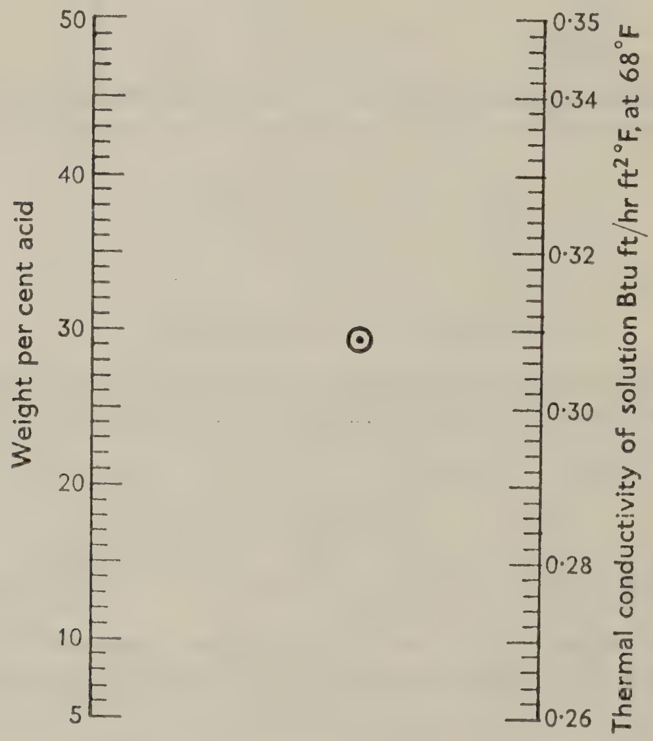


FIG. 5.—Thermal conductivity of orthophosphoric acid

Data have been recorded for more concentrated acid, as shown below:

*Thermal Conductivity of Phosphoric Acid*[366]

| Concentration Wt.-% $H_3PO_4$ | $t$ °C. | $10^4$ kcal./cm. sec. °C. | $10^7$ d$K$/d$t$ cal./cm. sec. °C.$^2$ |
|---|---|---|---|
| 87 | 23 | 10·63 | |
| | 63 | 11·48 | |
| | 103 | 12·35 | 22 |
| | 128 | 12·95 | |
| 100 | 23 | 10·38 | |
| | 63 | 11·30 | 21 |
| | 98 | 12·00 | |

## Dissociation Constants; Heat, Free Energy and Entropy of Ionization; Heat Capacity and Standard Entropies of Orthophosphoric Acid

Many measurements have been made of the dissociation constants of orthophosphoric acid, which ionizes in three stages:

$$\begin{gathered} H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \\ H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \\ HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \end{gathered}$$

Equations which represent recent and accurately determined values for the first[111] and second[112] dissociation constants are respectively:

$$-\log_{10} K_1 = 799{\cdot}31/T - 4{\cdot}5535 + 0{\cdot}013486T,$$

where $T$ is the absolute temperature (0°C. = 273·16° K.), for the temperature range 0–60°C., and

$$-\log_{10} K_2 = 2073{\cdot}0/T - 5{\cdot}9884 + 0{\cdot}020912T$$

over the temperature range 0–50°C. A similar equation for $K_2$, but with slightly different constants,[113] gives results which do not differ significantly from those given by the above equations up to 40°C., above which the values are somewhat higher. As the derived thermodynamic constants $\Delta H°$ and $\Delta C_p°$ are sensitive to variation in the temperature coefficient, these differ somewhat from the values derived from reference 112, but are given in parentheses, for comparison, in Table XXXI; the values for $\Delta F°$ and $\Delta S°$ are not affected.

At 25°C. the equations quoted above lead to the values:

$$\begin{aligned} K_1 &= 0{\cdot}711 \times 10^{-2} \\ K_2 &= 6{\cdot}31 \times 10^{-8} \end{aligned}$$

Simpler but less accurate equations for $K_1$, $K_2$ and $K_3$, have been given, based on thermodynamic data in the literature.[367]

The second dissociation constant, $K_2$, has been reported[114] as $6{\cdot}1 \times 10^{-8}$, $5{\cdot}82 \times 10^{-8}$, $5{\cdot}75 \times 10^{-8}$ and $5{\cdot}69 \times 10^{-8}$ at 60°, 70°, 80° and 90°C. respectively; in the region where the experimental observations overlap those of reference 112 they are in agreement.

Acceptable values for $K_3$, at 25°C., are $4{\cdot}73 \times 10^{-13}$ [115] or $4{\cdot}22 \times 10^{-13}$ [116]; previously reported values, lying between $10^{-13}$ and $10^{-12}$, are much less accurately established.

Extensive bibliographies of other values for the three dissociation constants have been compiled.[79, 312] Comparison of the dissociation constants of orthophosphoric acid with those of linear polyphosphoric acids having 2, 3, 6 and ~60 phosphorus atoms in the chain shows that the terminal hydrogens become more acidic and the last two dissociation constants approach a value of $10^{-8}$ as the chain length increases.[313]

The thermodynamic constants for orthophosphoric acid in water, at 25°C., derived from ionization data obtained during the dissociation constant determinations, are given in Table XXXI (see also [373]).

The relationship between the dissociation constants of orthophosphoric acid supports theories advanced for the calculation of such constants from equations involving the molecular structure and formal charges of oxyacid ions. The differences between the free energies of ionization, $\Delta F°$, of $H_3PO_4$, $H_2PO_4^-$ and $HPO_4^{2-}$, approximately 7 kcal., are characteristic of the general reactions[119, 120]:

$$\begin{gathered} X(OH)_2 \rightarrow HOXO^- + H^+ \\ HOXO^- \rightarrow {}^-OXO^- + H^+ \end{gathered}$$

This difference in energy corresponds, approximately, with the factor of $10^{-5}$ for the ratio of successive dissociation constants,

$$K_1 : K_2 : K_3 = 1 : 10^{-5} : 10^{-10}$$

proposed by Pauling.[121]

Another empirical equation for calculating dissociation constants, based on a more general formula, which includes terms for the formal charge on the central atom of the inorganic oxyacid and the number of non-hydroxyl oxygen atoms attached to it,[122] is:

$$\mathrm{p}K = 2{\cdot}1 + 4{\cdot}9(n-1).$$

For orthophosphoric acid (where $n = 1$, 2 or 3, corresponding to $K_1$, $K_2$ and $K_3$ respectively), this equation leads to values for $\mathrm{p}K_{1,2,3}$ of 2·1, 7·0 and 11.9, in fair agreement with those quoted in Table XXXI and also, it is claimed, for other oxyacids with similar structures.

*Table XXXI.—Thermodynamic Constants for Orthophosphoric Acid in Water, at* 25°C.

| | $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ | $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ | $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ |
|---|---|---|---|
| p$K$ | $\mathrm{p}K_1 = 2{\cdot}149$ [111]<br>2·12 [370] | $\mathrm{p}K_2 = 7{\cdot}199$ [112]<br>(7·200) [113]<br>7·20 [370] | $\mathrm{p}K_3 = 12{\cdot}325$ [116]<br>(12·375) [115]<br>12·36 [370] |
| $K$ | $K_1 = 0{\cdot}711 \times 10^{-2}$ [111] | $K_2 = 6{\cdot}31 \times 10^{-8}$ [112] | $K_3 = \begin{cases} 4{\cdot}22 \times 10^{-13} \text{ [116]} \\ 4{\cdot}73 \times 10^{-13} \text{ [115]} \end{cases}$ |
| $\Delta H°$ kcal./mole | −1·829 [111]<br>−1·9 [370] | +0·979 [112]<br>(1·003) [113]<br>+0·6 [370] | +3·50 [117]<br>+2·6 [370] |
| $\Delta F°$ kcal./mole | +2·934 [111]<br>+2·89 [370] | +9·822 [112]<br>+9·82 [370] | +16·30 [117]<br>+16·86 [370] |
| $\Delta S°$ g.-cal./°C./mole | −15·97 [111]<br>−16 [370] | −29·66 [112]<br>−31 [370] | −43·0 [117]<br>−48 [370] |
| $\Delta C_p°$ g.-cal./°C./mole | −36·8 [111] | −57·0 [112]<br>(47·8) [113] | |

Standard entropy, at 25°C., $S°$ g.-cal./°C./mole

| | |
|---|---|
| $H_3PO_4$(aq.) | 37·6 [118] |
| $H_2PO_4^-$ | 21·6 [118] |
| $HPO_4^{2-}$ | −8·0 [111-2] |
| $PO_4^{3-}$ | −51·0 [111-2] |

Predictions of dissociation constants can also be made, with some accuracy, from average p$K$ values derived from differential potentiometric titration curves.[123]

The dissociation of orthophosphoric acid possibly occurs by a mechanism similar to that proposed for nitric and sulphuric acids; that is by virtue of hydrogen bridges linking acid and water molecules. From a consideration of the rates of solution of zirconium and titanium in orthophosphoric acid solutions (5–85% $H_3PO_4$), it has been stated[124] that complete dissociation only occurs when there are more than 12 molecules ($m$) of water per molecule of $H_3PO_4$; that when $m < 4$ and $> 1$, the acid is partially ionized and that when $m \leqq 1$ the acid is undissociated, a conclusion at variance with evidence from conductivity measurements (q.v.). Solvation has also been invoked to account for discontinuities observed when other properties of aqueous orthophosphoric acid solutions, such as conductivity and viscosity, are correlated with concentration (q.v.). An alternative explanation,[371] which is supported by other observations,[357] is that species more acidic than $H_3PO_4$, such as the dimer $H_6P_2O_8$, are present. On the assumption that this ionizes to yield the triple ion $H_5P_2O_8^-$, equations can be derived which satisfactorily express the degree of dissociation of phosphoric acids in the concentration range 0·1–10 *m.* as a function of concentration, pH, and the concentrations of the various probable ionized and neutral species present in the solution.

To explain the rise in dissociation constant with increasing orthophosphoric acid concentration, the presence of $H_7(PO_6)$ molecules, with three totally dissociated hydrogen atoms has been suggested,[125–6] but this idea has not been investigated further by other workers.

The entropies, $S°$, of oxygenated ions of the form $XO_n^{-z}$ can be systematized on the basis of their size and charge by the relationship[127]:

$$S° = 43{\cdot}5 - 46{\cdot}5\,(z - 0{\cdot}28n),$$

where $z$ = the charge and $n$ = the number of oxygen atoms around the central nucleus, disregarding those present as hydroxyl groups. The entropies quoted in Table XXXI for $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$ are in good agreement with values calculated according to this equation, which also applies to other oxyanions such as $HSO_4^-$, $SO_4^{2-}$, $HSO_3^-$ and $SO_3^{2-}$.

It has been shown that a standard state can be chosen at any temperature, such that the partial molal entropies of any class of ions are linearly related to the corresponding entropies at 25°. Preliminary constants have been given which enable the calculation of entropy values up to 200°C. for $HPO_4^{2-}$ and $H_2PO_4^-$, using the equation:

$$\bar{S}^\circ_{t2} = a(t_2) + b(t_2)\bar{S}^\circ_{(t_1)}{}^{372}$$

From these values and the entropies at 25°C. it is possible to calculate corresponding values of the partial molal heat capacities for phosphate ions, using the equation:

$$[\bar{C}^\circ_{p2}]^{t2}_{25} = \frac{a_{(t2)} - \bar{S}^\circ_{25}[1{\cdot}000 - b_{(t2)}]}{\ln T_2/298{\cdot}2}$$

Heat capacities calculated in this way[373] are given below:

*Ionic partial molal heat capacities (g.-cal. mole$^{-1}$ deg.$^{-1}$)*

| *ion* | $\bar{C}^\circ_{p25}$ | $[\bar{C}^\circ_p]^{60}_{25}$ | $[\bar{C}^\circ_p]^{100}_{25}$ | $[\bar{C}^\circ_p]^{150}_{25}$ | $[\bar{C}^\circ_p]^{200}_{25}$ |
|---|---|---|---|---|---|
| $PO_4^{3-}$ | −226 | −200 | −216 | −205 | −227 |
| $HPO_4^{2-}$ | −132 | −118 | −129 | −138 | −146 |
| $H_2PO_4^-$ | −55 | −31 | −23 | −39 | −41 |

The effect of electrolytes on the dissociation constants of orthophosphoric acid has been investigated by a number of authors,[128–33, 312, 314] and equations are given for their evaluation in various alkali and alkaline-earth halide and sulphate solutions, in sea water and in urine. Generally speaking p$K_n$ decreases with increase in ionic strength and the effect of cations is in the increasing order $K^+$, $Na^+$, $Mg^{2+}$ and of anions $PO_4^{3-}$, $SO_4^{2-}$ and $Cl^-$.

The effect of pressure on the first dissociation constant, $K_1$, of orthophosphoric acid has been measured[134] at 25°C., the results being summarized in Table XXXII.

*Table XXXII.—$K_1$ (× 100) at 25°C. for Orthophosphoric Acid*

| Pressure, atm. | 1 | 500 | 1000 | 1500 | 2000 |
|---|---|---|---|---|---|
| $H_3PO_4$, molarity | | | | | |
| 0·00576 | 0·71 | 0·98 | 1·33 | 1·69 | 2·10 |
| 0·01 | 0·67 | 0·90 | 1·20 | 1·55 | 2·01 |
| 0·1 | 0·88 | 1·21 | 1·64 | 2·12 | 2·55 |

From this investigation, the change in partial molal volume of orthophosphoric acid on ionization was found to be −15·5 c.c./mole at 1 atm. and −10·7 c.c./mole at 2000 atm., whilst the change in compressibility on ionization was $-2{\cdot}4\times10^{-3}$ atm.$^{-1}$, c.c., mole$^{-1}$. A similar determination of the dissociation constants $K_1$ and $K_2$ at 22°C. and pressures up to 1000 kg./cm.$^2$ shows that the volume change on ionization at 1 atm. is 14·6–15·2 c.c./mole ($K_1$) and 22·0–28·1 c.c./mole ($K_2$) respectively.[315] Later data by the same author are in agreement with these values.[374]

Orthophosphoric acid is a slightly stronger acid in $D_2O$ than it is in water, according to calculations of the first and second dissociation constants from e.m.f. measurements, at 20°C., with the cell[135]:

$$D_2,Pt/H_3PO_4 \text{ in } D_2O/KCl(sat.), \text{ calomel.}$$

The corresponding p$K$ values are recorded in Table XXXIII, together with more recent values obtained by other methods.[316–7, 375]

*Table XXXIII.—Dissociation Constants of Orthophosphoric Acid in Water and* $D_2O$

| p$K_n$ | in $H_2O$ | in $D_2O$ | Temperature °C. | Reference |
|---|---|---|---|---|
| p$K_1$ | 1·983 | 2·188 | 20 | 135 |
| | 2·128 | 2·362 | 25 | 316 |
| | 2·145 | 2·350 | 25 | 375 |
| p$K_2$ | 7·207 | 7·666 | 20 | 135 |
| | 7·190 | 7·750 | 25 | 316,317 |

The effect of substituting a deuteron for a proton in the acid itself was to decrease the acid strength in water. It has been shown, using glass electrodes standardized for water solutions, that the pL (the generalized equivalent of pH, where L includes all isotopically different hydrogen ions) in a solvent of D atom fraction $n$ is given by[375]:

$$pL = (\text{meter reading}) + 0{\cdot}3314n + 0{\cdot}0766n^2$$

The first dissociation constant of phosphoric acid in hydrogen peroxide–water mixtures decreases non-linearly with $H_2O_2$ mole fraction. In this, it resembles acids such as acetic acid, rather than picric acid, where the variation is linear. The difference has been explained by solvation of the undissociated $H_3PO_4$ molecules which occurs to a much smaller extent in the internally hydrogen-bonded picric acid.[376] The dissociation of phosphoric acid in certain organic solvents has been studied[377–8] with the results given below:

| p$K$ | Water | 44·2% aq. acetone | solvent 50·9% aq. dioxan | 48·7% aq. dimethyl formamide | Acetic acid |
|---|---|---|---|---|---|
| p$K_1$ | 2·75 | 3·20 | 3·85 | 4·08 | 4·4 |
| p$K_2$ | 7·15 | 8·15 | 8·62 | 4·92 | — |
| p$K_3$ | 10·83 | 10·98 | 10·95 | 11·11 | — |
| Reference | 377 | 377 | 377 | 377 | 378 |

### Hydrogen-ion Concentration and Titration Curve

Because the dissociation constants of ionization of orthophosphoric acid are of quite different orders of magnitude, the hydrogen-ion concentration or pH titration curve is of considerable interest and three separate stages can be recognized when the acid is neutralized with an alkali, for example sodium hydroxide solution, corresponding to the formation of $NaH_2PO_4$, $Na_2HPO_4$ and $Na_3PO_4$ respectively. The graph in Fig. 6 shows the variation in pH when sodium hydroxide (0·0919 N.) is added to 100 c.c. of orthophosphoric acid solution (0·01277 M.) at 20°C.[136]

The first inflection, corresponding to the first stage in the neutralization, occurs at about pH 4·5, the second at about pH 9·0, but ionization at the third stage is too weak to give a distinguishable inflection and the course of the curve corresponds to the addition of excess sodium hydroxide. The titration curve for orthophosphoric acid can therefore be considered as consisting of the curves of three separate monobasic acids of widely differing strengths (see also Section XXVI, page 736).

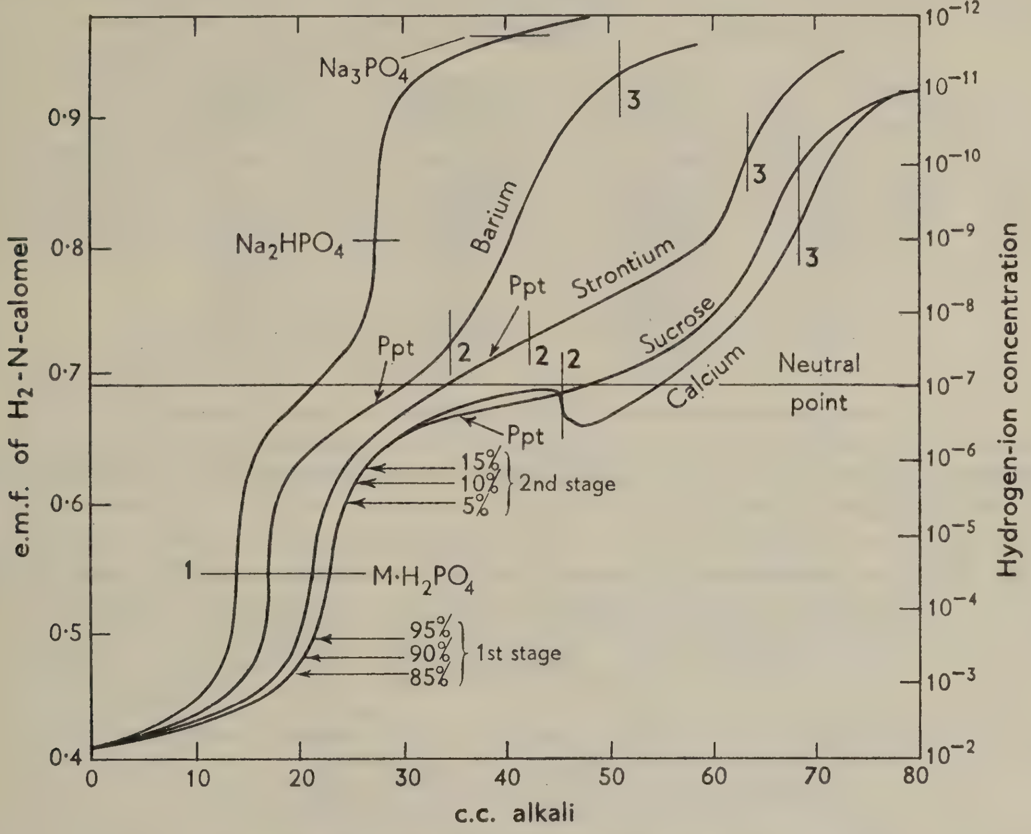


FIG. 6.—Titration curve of phosphoric acid

The choice of suitable indicators enables the inflection points to be observed visually, as well as by electrometric pH measurements, and affords a useful method for the differential titrimetric analysis of the soluble alkali metal phosphates (see Section XXXV, page 1257). If a phosphoric acid solution to be titrated against sodium hydroxide is first saturated with sodium chloride or sodium nitrate, it is claimed that sharper end points can be obtained, when azo-violet or thymolphthalein is used as indicator.[318] If the electrometric titrations are performed in very dilute solution, for example 0·001 to 0·0001 M., only the first stoicheiometric point in the neutralization can be recognized by an inflection in the curve.[137]

The neutralization of orthophosphoric acid by alkaline-earth hydroxides has also been studied; the pH-titration curves show breaks at the first stage of the neutralization, but thereafter insoluble phosphates are formed and other inflections are masked.[138] The volume changes, $\Delta V$, resulting from the mixing of aqueous solutions of phosphoric acid and alkalis supported the three-step dissociation mechanism for phosphoric acid. The maximum positive values of $\Delta V$ were at the $MH_2PO_4$ neutralization point, and the maximum negative values at the $M_3PO_4$ neutralization point.[379]

### Orthodeuterophosphoric Acid $D_3PO_4$; Physical Properties

The first preparation of orthodeuterophosphoric acid (53% $D_3PO_4$) dilute solution was concentrated to 83% $D_3PO_4$ by heating *in vacuo* at 54°C. in order to avoid pyrophosphoric acid formation,[22] but no measurements of physical properties were reported. A product, more nearly anhydrous, had $d_{20}^{4}=1{\cdot}890$, m.p. 38·4°C., and $n_D^{20}=1{\cdot}4430$.[139] The most reliable data, however, are given in Table XXXIV for orthodeuterophosphoric acid prepared by the addition of phosphoric oxide, purified by repeated sublimation *in vacuo*, to $D_2O$.[4]

*Table XXXIV.—Density,* $d_4^t$*; Viscosity,* $\eta$*; and Conductivity,* $K$*, of* $D_3PO_4$ *at 25° to 65°C.*

| °C. | $d_4^t$ g./cm.$^3$ | $\eta$ centipoises | $10^2K$ ohm/cm. |
|---|---|---|---|
| 25 | 1·9083 | 231·8 | 2·818 |
| 30 | 1·9042 | 182·4 | 3·378 |
| 35 | 1·9001 | 147·8 | 3·998 |
| 40 | 1·8959 | 118·7 | 4·632 |
| 45 | 1·8922 | 95·93 | 5·275 |
| 50 | 1·8888 | 77·44 | 5·940 |
| 55 | 1·8846 | 64·73 | 6·558 |
| 60 | 1·8807 | 55·18 | 7·261 |
| 65 | 1·8767 | 46·86 | 7·94 |

As seen in Table XXXV, $D_3PO_4$ has a higher m.p., $d_4^t$ and $\eta$, but a lower $K$ and $n_D^{20}$ than orthophosphoric acid.[4]

*Table XXXV.—Comparison of Some Physical Properties of* $H_3PO_4$ *and* $D_3PO_4$

| Property | $D_3PO_4$ | $H_3PO_4$ |
|---|---|---|
| m.p. °C. | 46·0 | 42·35 |
| $d_4^{25}$ | 1·9083 | 1·8683 |
| $\eta$ centipoises | 231·8 | 177·5 |
| $K$ ohm$^{-1}$ cm.$^{-1}$ | $2{\cdot}818\times10^{-2}$ | $4{\cdot}675\times10^{-2}$ |
| $n_D^{20}$ | 1·4430 | 1·4503 |

Unlike sulphuric acid, in which the activation energies of conduction and viscous flow are virtually unchanged by deuteration, there is a large influence when orthophosphoric acid is deuterated, especially on viscosity. Insufficient information is available to deduce reasons for the difference.[4]

## CHEMICAL PROPERTIES

### Action of Heat on Orthophosphoric Acid

When a dilute aqueous solution of orthophosphoric acid is heated water evaporates, the solution becomes more concentrated with respect to orthophosphoric acid and the boiling point increases slowly up to the composition corresponding to about 65% $P_2O_5$ (87·7% $H_3PO_4$). Thereafter the boiling point rises rapidly and the presence, in solution, of pyrophosphoric acid formed by the reaction:

$$2H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O$$

has been observed by paper and ion-exchange chromatographic analysis[100-1, 140] even though the $P_2O_5$ content has risen to only 68·8%, compared with 72·4% required for the anhydrous acid.

Liquid orthophosphoric acid itself has been shown by chromatographic analysis to contain about 12·7% of its $P_2O_5$ content in the form of pyrophosphoric acid and a corresponding proportion of 'free' water, possibly strongly solvated by the orthophosphoric acid, in accord with the equilibrium represented above; this conclusion is supported by conductivity measurements[4] and isotope exchange studies.[102]

On further heating, water continues to evaporate and condensation occurs according to the general equation:

$$nH_3PO_4 \rightleftharpoons H_{n+2}P_nO_{3n+1}+(n-1)H_2O$$

with the formation of mixtures of polyphosphoric acids, the proportions of the various constituents being related to the phosphoric oxide content of the mixture (see also Section XXVI, page 728).

The vapours above boiling orthophosphoric acid, b.p. 255°C., contain approximately 0·02 wt.-% $P_2O_5$; this proportion increases as the acid becomes more concentrated upon heating, until the azeotropic composition of 92·4% $P_2O_5$ is reached at about 864°C. at 760 mm. Hg, when liquid and vapour have the same composition.[32]

It has also been claimed that even at temperatures as low as 130°C. the partial pressure of $H_3PO_4$ in the vapour amounts to several thousandths of a mm. of Hg.[38]

## Anodic Behaviour of Metals in Orthophosphoric Acid

### COPPER

When a copper surface is anodically etched in concentrated aqueous solutions (> 10 N.) of orthophosphoric acid, it becomes as bright as if it had been polished, provided voltage and current density are regulated.[141] The mechanism of the process has been extensively studied on account of its industrial application.[145–51]

Over the range of voltage and current density in which electro-polishing occurs, the viscous layer formed on the surface of the anode contains phosphate ions which act as acceptors for the $Cu^{++}$ ions liberated by the current.[145] The reaction products concentrate in the hollows on the surface of the copper and passivate it, whereas the raised portions continue to be attacked, resulting in a general levelling and brightening of the surface.

The compounds responsible for the passivating effect are not definitely established, but the following have been suggested: $x\text{Cu}(H_2PO_4)_2,yH_3PO_4$,[152] $CuHPO_4$ and $Cu_2(PO_4)_3$,[142] or hydrated complexes of the type $CuH_2PO_4(OH)$. These are said to be in equilibrium with the acid in the solution on the one hand, and the surface oxide film on the metal surface on the other,[143–4] the formation of the complex being coincident with the appearance of the polished surface. In the critical polishing range the rate determining stage, that is the passage of phosphate radicals from solution to the anode, is diffusion controlled.[145–6,150–1]

Anodic polarization curves of copper in orthophosphoric acid[142,146,148–9] show several distinct stages in observed potentials: (*a*) when the product of the current density and the square root of the time in sec. is constant, (*b*) when the potential rises owing to the anode being electrolytically oxidized to $Cu_2O$, (*c*) another rise in potential when evolution of gaseous oxygen takes place on the anode surface and (*d*) a final levelling off in potential as the oxygen is evolved, the rate of evolution depending on whether the metal has been annealed or worked.[153] It is possible to differentiate between the stages of accumulation of reaction products and oxide film formation on the anode, by differential electrostatic capacity measurements on copper anodes immersed in 15 molar phosphoric acid.[148] Surface films, of the order of 100 A. thick, on copper electrolytically polished in orthophosphoric acid, have been reported to contain traces of unidentified phosphorus compounds in addition to oxides of copper.[154]

If single crystals of copper, sawn parallel to the (100), (110) and (111) faces, are polished anodically in orthophosphoric acid, *d* 1·53, the potentials of the three faces, when measured against the saturated calomel electrode after 3 min. immersion, are 0·342, 0·354 and 0·337 volts respectively; after much longer immersion in the polishing bath no difference is observed, all potentials being equal at 0·352 volts, showing that anodic polishing results in preferential formation of (110) faces.[155]

LEAD

As with copper, the anodic behaviour of lead in orthophosphoric acid can be considered in different stages. The electrolysis of 2·99, 22·80 and 40·5 N. $H_3PO_4$ with lead electrodes proceeds in steps. Firstly, when $Pb^{2+}$ ions pass into solution, forming a film of lead phosphate, accompanied by increase in potential and passivation of the anode; secondly, between 0·85 and 1·2 volts, when PbO and $PbO_2$ formation increases the degree of passivation, with fall in current density; and finally, electrolysis of $H_3PO_4$ at a potential of about 2·0 volts, accompanied by oxygen evolution.[156]

ZINC

In the anodic phosphatization of pure zinc in orthophosphoric acid solutions, as the current density increases, so does the concentration of $Zn^{++}$ ions in the neighbourhood of the anode, whilst that of the $H_2PO_4^-$ ions decreases. Further increase in current density results in a rise in the anode potential to the values required for reactions leading to the formation of $Zn_3(PO_4)_2$, $Zn(OH)_2$ and ZnO.[157]

MAGNESIUM

A theoretical study of the pH–potential diagrams for the system $Mg–H_3PO_4–H_2O$, confirmed by observation, indicates that magnesium is effectively passivated at pH less than 2 in solutions containing $10^{-6}$ g. ions of phosphate per litre.[158]

TITANIUM

Titanium is readily passivated electrochemically in orthophosphoric acid solutions.[159]

STEEL AND ALLOY STEELS

Carbon steels and alloy steels acquire a polish when used as anodes in electrolytic cells containing orthophosphoric acid[160–2]; generally speaking, the anodic attack proceeds in stages,[160–2] and additives, such as chromium trioxide, $CrO_3$, and sulphuric acid are often used to increase the polishing life of the electrolyte.[161]

## Action on Metals and Corrosion

Orthophosphoric acid is not nearly as corrosive as other common mineral acids, but the rate of attack on metals and alloys depends on the purity and concentration of the acid, the temperature and environment. Corrosion by orthophosphoric acid is often accompanied by the formation of protective or semi-protective films, so that large variations in the rate of attack on the same metal may be observed under different conditions. Aeration also increases the rate of corrosion of most metals and alloys.

The extensive literature concerned with corrosion by orthophosphoric acid is to be found mainly in technical journals and useful collections of data for a wide range of metals and alloys are available.[163–76, 319]

ALUMINIUM

Orthophosphoric acid solutions are inherently corrosive to aluminium and its alloys[177–9]; penetration rates are as follow (Table XXXVI).

*Table XXXVI.—Corrosion Rates for Aluminium in Orthophosphoric Acid*

| % $H_3PO_4$ | Temperature °C. | Penetration rate inches per year |
|---|---|---|
| 42 | 15 | 0·292 [179] |
| 76 | 15 | 0·730 [179] |
| 85 | 95 | 0·63 [164] |

However the addition of small quantities of phosphoric acid reduces the corrosion of aluminium-clad fuel elements in pressurized water reactors, although heavy deposits are formed.[320]

### ANTIMONY

At 15°C. antimony suffers moderate attack by orthophosphoric acid solutions (up to 76% $H_3PO_4$), the corrosion rate being of the order of 0·01 in./year.[179]

### BISMUTH

Bismuth is unattacked under the conditions described for antimony[179] because of the formation of a protective layer of bismuth phosphate.

### CADMIUM

Cadmium is moderately attacked by orthophosphoric acid at 15°C., the rate being equivalent to a penetration of approximately 0·02 in./year for 76% $H_3PO_4$.[178] The rate of solution of cadmium in more dilute acids increases with time over a period of a few hours[180]; for example, in 0·1N. $H_3PO_4$ the loss expressed in mg./cm.$^2$ increases from 0·35 to 1·4 at 20°C., from 0·49 to 2·2 at 40°C. and from 0·54 to 3·0 at 60°C. Other similar data for 0·5N., N. and 2N. $H_3PO_4$ are available in the same reference, the rate of solution increasing with rise in both acid strength and temperature.

### COPPER (AND ALLOYS)

Copper and its alloys resist attack by orthophosphoric acid moderately well as long as the content of dissolved oxygen, or of oxidizing impurities, such as ferric compounds, is fairly low.[164, 172, 179, 182] In quiescent, unaerated 76% orthophosphoric acid at 20°C. copper corrodes at a rate equivalent to a penetration of 0·008 in./year[178]; under aerated and stirred conditions at higher temperatures, the rate of corrosion by all grades of orthophosphoric acid may rise to many times this value.

Data on copper alloyed with zinc, tin, nickel, aluminium and silicon are available.[172, 183–6, 321]

Copper shows relatively good corrosion resistance to solutions of orthophosphoric acid at 1000 lb./sq. in. pressure and at 285°C.,[187] whilst in the absence of oxygen it is not appreciably corroded by dilute orthophosphoric acid in steam heated above its critical temperature to 4550 lb./sq. in. and 440°C.,[188] i.e., conditions under which copper–silver alloys are rapidly attacked.

### GOLD

Gold and its alloys with platinum, silver[189] and silver with palladium[190] are practically unattacked by orthophosphoric acid over a wide range of temperature and concentration of acid. Electro-plating of iron and steel is possible with the metal and many of its alloys.

### LEAD

As a consequence of the formation of thin films of insoluble lead phosphate in pure and of lead sulphate in crude orthophosphoric acid solutions, the resistance shown by lead to corrosion by the former is very satisfactory and to the latter exceptionally good.[165, 178]

The corrosion rates in Table XXXVII have been reported for the pure acid,[175] the rates of attack by impure acid, for example that produced by the gypsum process, being much less.

Other data are available for different environments and acid concentrations.[165, 191] Antimonial lead, containing about 7% of antimony, does not show the same resistance as pure lead.[165, 179]

MAGNESIUM

Magnesium is attacked extremely rapidly by both pure and impure orthophosphoric acids.[178]

MOLYBDENUM

Molybdenum is very little affected by boiling phosphoric acid at concentrations in the range 1–85% $H_3PO_4$.[322]

NICKEL

Nickel shows moderate resistance to attack by pure dilute orthophosphoric acid in the cold,[164,178] but hot concentrated solutions are much more corrosive; for example, at 95°C. penetrations of about 0·7 in./year for 85% $H_3PO_4$ have been recorded.[164,174]

*Table XXXVII.—Corrosion Rates for Lead in Orthophosphoric Acid*

| % $H_3PO_4$ | Temperature °C. | Penetration rate inches per year |
|---|---|---|
| 72 | 20 | 0·0043 |
| 10 | 81 | 0·0014 |
| 25 | 81 | 0·043 |
| 50 | 81 | 0·065 |

The high nickel alloys, especially those containing molybdenum or chromium, exhibit a high degree of corrosion resistance to orthophosphoric acid of all concentrations. At room temperature the rate of attack is less than 0·002 in./year for any type of alloy and for all concentrations of acid; at higher temperatures nickel alloys containing molybdenum are somewhat more resistant than others.[163,174,192]

Useful summaries of corrosion data are available. [163–4,174]

NIOBIUM

Niobium has a high degree of resistance to attack by unaerated, unstirred 85% $H_3PO_4$ at temperatures in the region of 25°C., the penetration recorded over a 36-day test being only 0·00002 in./year.[181] Niobium also shows good resistance to 3–10% $H_3PO_4$ at temperatures up to 300°C., but the protective film which forms under these conditions does not prevent hydrogen embrittlement of the metal.[323]

PLATINUM

Platinum and its alloys with gold are virtually unattacked by orthophosphoric acid (cf. polyphosphoric acids) at concentrations up to 100% $H_3PO_4$, and up to their boiling points; their use for electroplating iron and steel to improve corrosion resistance has been suggested.[189,323]

SILVER

Silver is not attacked by either pure or impure orthophosphoric acid in the cold,[178,189,193] nor is it seriously attacked at temperatures up to 200°C., except when aerated.[182,189,194] Under extreme conditions of temperature, up to 300°C., alloys with copper or nickel are more resistant than silver itself,[182] for which a penetration rate of only 0·007 in./year in 85% $H_3PO_4$ at 249°C. and at 1000 lb./sq. in. pressure has been reported.[187] At even higher temperature and pressure, 440°C. and 4550 lb./sq. in., pure silver and a fine-grained alloy of silver containing 1% of nickel are scarcely attacked, but alloys with higher nickel contents fail through attack on the nickel phase.[188] A silver–silicon alloy, containing 1–2% of silicon, is reported to be corrosion resistant to orthophosphoric acid up to 400°C.[195]

### IRON AND STEEL

Pure iron is readily attacked by dilute or concentrated orthophosphoric acid,[178] the rate of attack being reduced somewhat by the inhibiting effect of the organic impurities present in some concentrated impure acids.[164] Generally speaking, however, crude orthophosphoric acids are more corrosive towards iron and its alloys, on account of the presence of fluoride, chloride or sulphate ions.

The corrosion of ferrous alloys by orthophosphoric acid has received much study on account of the extensive use of such alloys as materials of construction for processes in which the acid is made on an industrial scale. Detailed data on the corrosion rates of a wide range of steels and other ferrous alloys are to be found in the more general review papers referred to earlier.[163–6, 171, 173, 176, 323] The extent of corrosion varies greatly depending on the type of alloy, the purity and concentration of the orthophosphoric acid, the temperature and the conditions of exposure to attack.

However, the typical behaviour of several classes of alloys can be summarized. Cast iron is, in general, subject to severe corrosive attack by pure and crude orthophosphoric acid solutions.[163] Moderate resistance is shown by stainless steels containing up to about 18% of chromium,[164, 179, 196] but above this percentage excellent resistance has been reported and especially so when 10–15% of nickel and 2–4% of molybdenum are also present in the alloys.[163–4, 171, 179, 186, 192, 196–204] A 25% Cr, 5% Ni stainless steel is unstable in phosphoric acid because of periodic depassivation in some specimens, which is promoted by chloride ion.[380] The high alloy stainless steels, containing about 20% of chromium and 30% of nickel, together with a little molybdenum and copper, are practically unattacked, even under the most severe conditions and in the presence of impure acid.[163, 171, 192, 196, 205, 206, 380–1] Steels stabilized by titanium or niobium, and with low carbon contents, are claimed to be more resistant to the type of corrosion attributable to weld-decay at gas or electric-welded joints when immersed in orthophosphoric acid solutions.[163, 171, 196, 202] The high silicon irons, namely those containing about 14% of silicon and 1% of carbon, show good resistance to pure orthophosphoric acid up to about 100°C., but not towards acids with fluorine compounds as impurities.[163, 176, 202, 204, 324]

Although iron is usually dissolved by orthophosphoric acid, under certain conditions in dilute acid solutions a protective coating of phosphate can be formed on the metal surface, thus effectively preventing further attack.[207] A similar phenomenon has been demonstrated in stainless steels.[382] The initial reaction can be represented by the equation:

$$\mathrm{Fe + 2H_3PO_4 = Fe(H_2PO_4)_2 + H_2}$$

As the concentration of iron in solution increases, the following equilibria can occur[208–9]:

$$\begin{aligned}&\mathrm{Fe(H_2PO_4)_2 \rightleftharpoons FeHPO_4 + H_3PO_4}\\&\mathrm{3FeHPO_4 \rightleftharpoons Fe_3(PO_4)_2 + H_3PO_4}\\&\mathrm{3Fe(H_2PO_4)_2 \rightleftharpoons Fe_3(PO_4)_2 + 4H_3PO_4}\\&\mathrm{2FeHPO_4 + Fe \rightleftharpoons Fe_3(PO_4)_2 + H_2}\end{aligned}$$

with the ultimate formation of relatively insoluble secondary and tertiary phosphates of iron, which deposit as a thin layer on the metal surface. Other metals, such as manganese and zinc, behave in a similar manner and this principle has been utilized in the so-called 'phosphatization' processes used commercially for producing paint-adherent protective coatings on several metals. Both the theoretical and practical aspects of these processes have been discussed and reviewed.[208, 210–1]

### TANTALUM

Tantalum is inert to all concentrations of pure orthophosphoric acid up to 175°C. In the presence of more than 10 p.p.m. of fluorides, however, embrittlement and pitting occur; sulphates also accelerate corrosion.[163–4, 166, 170, 181, 187, 323]

Chlorides, however, do not accelerate the corrosion of commercially pure tantalum.[383] An alloy of Ta (40%), Nb (46%), Ti (10%) and Ni (4%), resisted the attack of phosphoric acid at 200°C.[384]

### TIN

Tin is readily attacked by pure and crude orthophosphoric acids, the reported corrosion rates[163, 178] being given in Table XXXVIII.

*Table XXXVIII.—Corrosion Rates for Tin in Orthophosphoric Acid*

| | Concentration $H_3PO_4$ % | Temperature °C. | Penetration inches per year |
|---|---|---|---|
| Pure $H_3PO_4$ | 76<br>85 | 15<br>93 | 0·01<br>0·88 |
| Crude $H_3PO_4$ | 76<br>62 | 15<br>98 | 0·24<br>1·14 |

### TITANIUM

Titanium is fairly resistant to attack by pure 10% orthophosphoric acid at 80°C. and by 85% acid at 25°C.,[212] a penetration rate of 0·007 in./year being recorded for the latter.[181] In the higher acid concentration ranges and at higher temperatures, titanium is subject to increased attack and is not satisfactorily resistant, at 60°C., to solutions containing more than 3% $H_3PO_4$. At 35°C. the rate of penetration increases from 0·002 to 0·028 in./year as the concentration rises from 30 to 80% $H_3PO_4$.[213, 322] Arc-melted titanium is said to be more resistant to orthophosphoric acid solutions than powder-metallurgy titanium, and alloys with 14% of zirconium have increased resistance to this medium.[214] Niobium (up to 50%) also increases the resistance of titanium to attack by phosphoric acid,[385] but aluminium–titanium alloys are less resistant.[386] Measurements at 40°, 50° and 60°C. show that the rate of solution of titanium in 6–28 N. orthophosphoric acid can be regarded as approximately proportional to its concentration and that the activation energy of the reaction is 15·67 kcal./mole.[215, 325]

### TUNGSTEN

Tungsten is little attacked by boiling phosphoric acid solutions in the range 1–85% $H_3PO_4$.[322]

### ZINC

Zinc is very readily attacked by solutions of both pure and crude orthophosphoric acid at all concentrations and all temperatures.[164, 178]

### ZIRCONIUM

The corrosion resistance of zirconium to orthophosphoric acid of all concentrations is very high at temperatures up to 60°C.[181, 216–7] At 100°C. the corrosion resistance falls off rapidly with increasing acid concentration, as Table XXXIX shows.[212, 322]

*Table XXXIX.—Corrosion Rates for Zirconium in Orthophosphoric Acid at* 100°C.

| Concentration, % $H_3PO_4$ | 60 | 70 | 80 | 85 |
|---|---|---|---|---|
| Penetration in inches per year | 0·004 | 0·008 | 0·024 | 0·044 |

Alloys of zirconium and niobium show satisfactory resistance to phosphoric acid (up to 40%) at 100°C. for 100 hr.[326]

### INHIBITORS FOR REDUCING THE ATTACK ON METALS BY ORTHOPHOSPHORIC ACID

The extent to which metals are attacked by orthophosphoric acid may be reduced by small amounts of inhibitors dissolved in it. Of the inorganic substances suggested for this purpose, pentavalent arsenic[164, 218] is very effective in preventing attack on steel, whilst chromates are reported as inhibiting the attack on aluminium and light metal alloys.[219, 220] The addition of 0·05–2·5 g./l. of copper to the acid is said to reduce the corrosion of austenitic steels containing chromium and nickel.[221] Many organic inhibitors have been reported, most of which are nitrogeneous compounds such as amines,[222–4] nitriles[224] or thioureas[225]; aldehydes (in conjunction with ionizable halides),[226] pine oil and glue[164] have also been mentioned. As the presence of sulphuric, fluosilicic and hydrofluoric acids tends to increase the corrosive effect of orthophosphoric acid,[164] the addition of more inhibitor is required with crude acid than with pure acid to obtain the same effect.

The corrosion of copper or brass by phosphoric acid is inhibited by furfuraldehyde[387] or mercaptobenzthiazole.[388]

## Radioactive and Isotopic Exchange Reactions with Orthophosphoric Acid

Radioactive phosphorus, $^{32}P$, in orthophosphoric acid does not exchange in aqueous solution with other phosphorus compounds, such as phosphorous acid,[227] hypophosphorous acid,[228] pyrophosphate, hypophosphate or other condensed phosphates,[229–31] phosphoric acid esters,[232] nor with biological phosphates.[233]

Radioactive phosphorus can therefore be employed as a tracer in analytical procedures, and when it does appear in a phosphorus compound, other than the original, it may be assumed that the second must have been produced from the first.

Isotopic exchange of $^{18}O$ between orthophosphoric acid and water in which it is dissolved does, however, take place.[102, 234–5] The rate of exchange, reported to be lower than that observed between water and phosphorous or hypophosphorous acid,[234] has been extensively studied. The rate of exchange of $^{18}O$ between orthophosphoric acid and water was measured at various temperatures as a function of the acid concentration, taking into account the fact that some pyrophosphoric acid is present in nominal compositions just below 100% $H_3PO_4$,[102] with the results shown in Table XL. The equation representing the exchange is:

$$H_2O^* + H_3PO_4 \rightleftharpoons H_2O + H_3PO_4^* \quad (1)$$

*Table XL.—Exchange Rates of* $^{18}O$ *between Water and Orthophosphoric Acid, g. atoms/l. sec.* × $10^4$

| $H_3PO_4$ $f$ | °C. | | | | | | | Energy of activation kcal./mole |
|---|---|---|---|---|---|---|---|---|
| | 25 | 40 | 60 | 80 | 90 | 100 | 110 | |
| 8·8 | — | — | — | — | 0·141 | 0·341 | 0·78 | 26·5 |
| 12·2 | — | — | 0·0286 | 0·221 | 0·511 | 1·14 | 2·62 | 24·0 |
| 15·1 | — | 0·0137 | 0·106 | 0·672 | 1·59 | 3·45 | 8·65 | 23·1 |
| 17·8 | 0·0148 | 0·070 | 0·462 | 2·05 | 4·53 | 9·47 | — | 19·7 |

$f$=formality of solution, which is molarity corrected for presence of pyrophosphoric acid, where necessary.

An alternative path for exchange, in the more concentrated acids, is the equilibrium:

$$2H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O \quad (2)$$

and the rate of change of reaction shown in (2) was found to be almost identical with the isotope exchange rates (see Table XLI).

*Table XLI.—Comparison between* $H_4P_2O_7$ *Hydrolysis Rate and* $H_3PO_4$–$H_2O$ *Isotopic Exchange Rate*

| °C. | $H_3PO_4$ *f* | $H_4P_2O_7$ hydrolysis rate mole/l. sec. | $H_3PO_4$–$H_2O$ isotope exchange rate g. atoms/l. sec. |
|---|---|---|---|
| 25 | 18·0 | $1{\cdot}5 \times 10^{-6}$ | $1{\cdot}9 \times 10^{-6}$ |
| 60 | 7·8 | $5 \times 10^{-5}$ | $4{\cdot}6 \times 10^{-6}$ |

It is claimed[102] that the observed exchange rates can be represented satisfactorily by an equation of the form:

$$\text{(3)} \qquad \text{rate} = k_1a_1a_w + k_2a_1^2 + k_3a_1^3/a_w$$

where $a_1$ and $a_w$ are the activities of the orthophosphoric acid and water, and $k_1$, $k_2$ and $k_3$ have the values $3{\cdot}8 \times 10^{-5}$, $2{\cdot}4 \times 10^{-7}$ and $4{\cdot}5 \times 10^{-12}$ g. atom/l. sec. respectively. The first term is important at low concentrations of $H_3PO_4$, the second at higher concentrations and the third only at the highest concentrations.

The mechanism of the isotopic exchange is believed to involve direct replacement of oxygen in $H_3PO_4$ (first term in equation (3)) and the reversible formation and hydrolysis of $H_4P_2O_7$ and possibly $H_5P_3O_{10}$ (second and third terms). The interaction of undissociated $H_3PO_4$ with its conjugate acid $H_4PO_4^+$ may be involved in these reactions.[327]

Isotopic dilution analysis[102] confirmed the presence of pyrophosphoric acid in very concentrated orthophosphoric acid solutions, the results agreeing with those obtained by chromatographic analysis[100-1] and conductivity measurements.[4]

In contrast to this, it appears that the mechanism of $^{18}O$ exchange at higher pH is analogous to the hydrolysis of monoalkyl phosphates, involving a first order attack of $H_2{}^{18}O$ on the monoanion $H_2PO_4^-$. Above pH 0 nucleophilic catalysis by anions of strong acids ($Cl^-$, $ClO_4^-$) was absent, but at higher phosphoric acid concentrations the perchlorate anion strongly catalyzes the exchange, perhaps by a salt effect[327] or through the formation of the species $P(OH)_4^+$.[358]

## The Reactions of Orthophosphoric Acid

### REACTION WITH HALOGEN ACIDS AND HALIDES

Orthophosphoric acid reacts with hydrogen fluoride according to the equilibrium:

$$H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$$

the reaction proceeding further towards the right in the presence of strong acids, such as perchloric, nitric, sulphuric or benzenesulphonic acid, which remove free water from the system.[236] On the other hand monofluorophosphoric acid is completely hydrolyzed, according to the reverse reaction, when boiled in aqueous solution.[237]

Dry gaseous hydrogen chloride is absorbed by pure orthophosphoric acid to the extent of 8% by weight; such solutions, with respect to pH and conductivity, behave as if the compound $H_4PO_4Cl$ were present. This compound, soluble in $H_3PO_4$, slowly decomposes with the evolution of HCl if the orthophosphoric acid is allowed to crystallize out at room temperature.[238]

The isobaric absorption of hydrogen chloride, at 28·7–747·7 mm. pressure, and of hydrogen bromide, at 73·0–670·5 mm. pressure, by orthophosphoric acid (81·5–99·5% $H_3PO_4$) at temperatures between 50° and 160°C., has been studied and the heats of absorption measured. For HCl this varies from −2700 to −6 g.-cal./mole between 50° and 160°C. and from −2600 to −1100 g.-cal./mole between 70° and 160°C. for HBr. The diminution in heat of absorption with temperature is attributed to interaction between halogen acid and orthophosphoric acid,[239] for example:

$$3HCl + H_3PO_4 \rightleftharpoons POCl_3 + 3H_2O$$

Highly soluble calcium chloride, bromide and iodide form a series of double salts with orthophosphoric acid, under the specific conditions shown in Table XLII.[240]

*Table XLII.—Double Salts formed between Orthophosphoric Acid and Calcium Halides*

| Formula | Name | % Calcium halide | Temperature °C. |
|---|---|---|---|
| $CaCl_2,Ca_3(PO_4)_2$ | chlorospodiosite | 52–54<br>or 52–61 | 150<br>175 |
| $CaCl_2,3Ca_3(PO_4)_2$ | chloroapatite | 44–52 | 175 |
| $CaCl_2,Ca(H_2PO_4)_2,2H_2O$ | monocalcium chlorophosphate | not < 41–52 | 25–125 |
| $CaBr_2,Ca(H_2PO_4)_2,8H_2O$ | monocalcium bromophosphate | 53–58<br>or 55–56 | 0<br>25 |
| $CaBr_2,Ca(H_2PO_4)_2,2H_2O$ | monocalcium bromophosphate | 60–66 | 25–175 |
| $CaI_2,Ca(H_2PO_4)_2,8H_2O$ | monocalcium iodophosphate | — | at room temperature |

The formation of $CaCl_2,Ca(H_2PO_4)_2,2H_2O$ at 25°C. was previously reported in a physico-chemical study of the system $CaO–P_2O_5–HCl–H_2O$,[241] and its preparation as an intermediate in the production of calcium hydrogen phosphate, $CaHPO_4$, has been described.[242]

The reaction between magnesium chloride and orthophosphoric acid in 12·5, 25 and 50% excess over the stoicheiometric proportions required to form $Mg(H_2PO_4)_2$, has been studied at 49°, 75° and 95°C.; a higher temperature favours the removal of chloride ions as hydrogen chloride, for example:

$$2H_3PO_4 + MgCl_2 = Mg(H_2PO_4)_2 + 2HCl$$

and the mean activation energy of the process is reported to be 14·34 kcal./mole. With a 50% excess of orthophosphoric acid at 95°C., conversion is complete in 215 min.[243] Similar reactions occur with other alkali and alkaline-earth salts, the product obtained depending on the excess of acid used and the final temperature to which the reaction mixture is submitted.

### REACTION WITH OXYACIDS

Orthophosphoric acid and perchloric acid form a compound $H_3PO_4,HClO_4$, m.p. 46°–47°C., the electrolysis of which in methyl nitrite indicates that $H_3PO_4$ forms a positive ion, i.e. has basic properties, relative to the stronger acid $HClO_4$, in this solvent. The reaction:

$$PO(OH)_3 + HClO_4 = \overset{+}{P}(OH)_4ClO_4^-$$

may be compared with[244]:

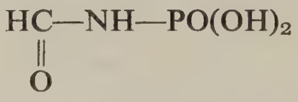
$$NH_3 + HClO_4 = NH_4^+ClO_4^-$$

The heat of solution of the complex in methyl nitrite is 13·9 kcal./mole. The *X*-ray diffraction pattern shows no resemblance to other perchlorates and the name tetrahydroxophosphor(V) perchlorate has been proposed.[245]

In a similar way infra-red,[328], N.M.R.[329] and other[330,343,365,369] evidence has been adduced for the existence of protonated species such as $\overset{+}{P}(OH)_4$ in the system $H_2SO_4$–$H_3PO_4$–$H_2O$. Other authors have interpreted electrical conductivity, viscosity, density, and refractive index isotherms as showing that no such interaction occurs.[331] Further study of the system is obviously desirable.

### REACTION WITH HYDROGEN CYANIDE

When 100% orthophosphoric acid and hydrogen cyanide are kept in a sealed tube for several weeks at room temperature, a viscous liquid separates which eventually crystallizes as a white amorphous solid. The composition corresponds to the formation of $H_3PO_4$,HCN which, from the mechanism of its breakdown on heating to form carbon monoxide and monoammonium dihydrogen phosphate, is believed[246] to have the structure:



$$\underset{\overset{\|}{O}}{HC}—NH—PO(OH)_2$$

### REACTIONS WITH GRAPHITE

Whilst under most conditions of concentration and temperature graphite and carbon are not attacked by orthophosphoric acid, the former, in the presence of an oxidizing agent such as chromic acid, begins to react at 80°–100°C. to form a brown material the *X*-ray powder diagram of which resembles that of the blue graphite–sulphuric acid compound which contains 24 carbon atoms to 1 molecule ion $HSO_4^-$. It is believed that in such compounds the hexagonal planes of the graphite are spread by the insertion of acid layers between them.[247] The rapid rate of wet oxidation of highly graphitized samples of carbon by orthophosphoric acid and bichromate possibly involves graphite–phosphate formation and decomposition.[248] Similar indications of 'salt' formation are obtained during the anodic oxidation of well-ordered specimens of pyrolytic graphite.[364]

### COMPLEXING OF METAL IONS BY ORTHOPHOSPHORIC ACID

The complexing of metal ions by orthophosphoric acid is well known and has been used in analytical chemistry for many years.[249–51] For example, the decolorizing action of orthophosphoric acid on the ferric ion is said to be due to the formation of the stable, soluble, colourless $FeHPO_4^+$ ion.[252–3] Other evidence[254] cited for the existence of soluble ferric ion–orthophosphoric acid complexes includes (*a*) the lowering of the oxidation potential of the ferrous-ferric system in the presence of orthophosphoric acid,[255] (*b*) the enhanced conductivity of mixtures of ferric salts and orthophosphoric acid above that expected from the sum of the constituent conductivities,[256] (*c*) the fact that the presence of orthophosphoric acid causes the reversible iodometric oxidation of the ferrous ion to proceed to completion,[257] and (*d*) the interference shown by orthophosphates to the colour developed by ferric and thiocyanate ions. It has also been reported that there is evidence for anionic orthophosphate–ferrate complexes from the movement of iron to the anode in transference measurements.

Various formulations for the complexes have been proposed, for example:

$[Fe(PO_4)_2]^{3-}$ and $[Fe(PO_4)_3]^{6-}$ [259]
$[FeHPO_4]^{+}$ [252–3]
$[FeH_2PO_4]^{2+}$ [260]
$[Fe(PO_4)Cl_3]^{3-}$ in the presence of chloride ions[256,261]

but it has also been stated that the complex(es) cannot be represented stoicheiometrically.[257] Ion-exchange studies[254] have shown the existence in solution of a complex containing three orthophosphate groups per iron atom, whilst breaks in the conductimetric titration curves of ferric chloride and orthophosphoric acid[262] indicate both $Fe(HPO_4)^+$ and $Fe(HPO_4)_2^-$ ions. Spectrophotometric studies have been used to study the stability of some of the complexes,[253, 263] crystalline salts of several of the phosphato-ferric acids have been isolated[255, 259, 264–5] and the phase diagram of the system $Fe–H_3PO_4–H_2O$ has been described.[255]

Aluminium, like iron, forms quite stable complexes with orthophosphoric acid,[255, 260] for some of which dissociation constants have been reported.[266]

Complexes between orthophosphoric acid and the following metals have also been mentioned: copper,[267] cobalt,[268] silver,[269] thorium,[270] plutonium,[271] uranium,[272] iridium[332] and even calcium.[273]

Some studies have also been made of the soluble complexes formed between the alkali and alkaline-earth metals and orthophosphoric acid; measurements of the dissociation constants for the 1 : 1 complexes, $MHPO_4$, show that they are not so stable as, for example, the iron and aluminium complexes referred to above.[274–5] The subject is fully discussed by Van Wazer and Callis.[258]

The formation of an extremely viscous fluid when 1·0–1·5 moles of alumina are dissolved in 1·0 mole or orthophosphoric acid is interesting. On drying, the solution forms an amorphous solid which can be dispersed again in water to give a solution with the original viscous properties.[276] It has been suggested that the colloidal nature of such solutions is due to the formation of polymeric aggregates, in which $PO_4$ tetrahedra are held together by aluminium ions. The degree of aggregation and stability of these polymers, like those of the heteropolyacids of phosphorus, are pH-dependent, being greater in a highly acid medium.[277] Excess of phosphoric acid reacts with corundum, even at 100°–120°C., giving aluminophosphates similar to those formed from hydrated alumina. Hydrated aluminophosphates, $Al_2O_3,3P_2O_5$, and the quartz, tridymite, and cristobalite forms of $AlPO_4$, together with *X*-ray diffraction lines belonging to an unidentified compound, can be detected at various higher temperatures. A glassy phase is formed at 1400°C.[389]

On the evidence of solubility and vapour pressure measurements,[278–80] soluble borophosphoric acids have been reported, but the nature of such complexes and their salts is as yet little understood; they probably contain a B–O–P network, similar to that believed to exist in boron phosphate, $BPO_4$.

Solubility evidence has also been invoked to support the belief that arsenophosphoric acids exist in solution, although the corresponding compounds cannot be isolated.[281]

### REACTION WITH SILICA

Silica, in any of its forms, when heated with orthophosphoric acid, dissolves to an extent dependent on its state of sub-division and on the temperature and concentration of the acid. The amorphous hydrated precipitate which first separates from solution dehydrates on further heating and eventually becomes crystalline.

A hydrated compound, $2P_2O_5,SiO_2,4H_2O$, has been described; it is formed by the action on silica of orthophosphoric acid previously heated to 250°–300°C.,[282] or by raising to 200°C. and thereafter maintaining at 125°C. for about 300 hr. a mixture of silica gel and orthophosphoric acid.[283] It has been suggested [283] that the compound can be regarded as a heteropoly-acid of the type $H_8[Si(PO_4)_4]$, but direct proof of octabasicity is lacking since it decomposes in warm water, alkali and acid, with the separation of silica. The clear solution obtained in cold water contains colloidal silica and, from electrical conductivity measurements, the compound is thought to be completely dissociated in dilute solutions.

Several references have been made to an anhydrous compound with the composition $P_2O_5,SiO_2$[282, 284–5] which separates when phosphoric acid and silica are heated together in sealed tubes or for prolonged periods at high temperatures. From a study of its behaviour in molten silver nitrate, when silver pyrophosphate is formed, it has been claimed[285] that $P_2O_5,SiO_2$ should be considered as neutral silicon pyrophosphate, $SiP_2O_7$, a conclusion supported by *X*-ray structural evidence.[286] The occurrence of the pyrophosphate structure is not surprising, since at the temperature of preparation the phosphoric acid would consist of a mixture of polyphosphate species.

When colloidal solutions of silica are evaporated with various proportions of phosphoric acid and the products dried at 110°C., gelatinous solids are formed; prolonged drying at 200°C. does not alter their composition, but the compounds become anhydrous. Evidence from composition, behaviour with molten or powdered silver nitrate and *X*-ray powder diffraction analysis using internal standards,[285] indicates that the compounds shown in Table XLIII can be formed.

*Table XLIII.—Compounds formed from Colloidal Silica and Phosphoric Acid*

| Molar ratio $P_2O_5/SiO_2$ | Compound | Preparation and properties |
|---|---|---|
| 1·0 | $P_2O_5,SiO_2,H_2O$<br>$Si(HPO_4)_2$<br>Silicon acid orthophosphate | From solutions containing $P_2O_5/SiO_2 \geqq 1$<br>Formed only when drying temperature is held below 180°C.; converts to $SiP_2O_7$ on further heating |
| 1·0 | $P_2O_5,SiO_2$ $SiP_2O_7$<br>Neutral silicon pyrophosphate | From solutions containing $P_2O_5/SiO_2 \geqq 1$<br>Exists in two, or possibly three allotropic forms, according to method of preparation |
| 0·66 | $2P_2O_5,3SiO_2$<br>$Si_3(PO_4)_4$<br>Neutral silicon orthophosphate | From solutions containing $P_2O_3/SiO_2 < 1$<br>No change in *X*-ray pattern by heating to 900°C. |

Attempts to isolate compounds with molar ratio $P_2O_5/SiO_2 = 2$ did not succeed.[285]

If phosphoric acid is heated in Pyrex glass containers at 300°C., the white mass which eventually forms is said to be neutral silicon orthophosphate.[285] Borosilicate glass is, however, unaffected by boiling 30–40% phosphoric acid.[333] Attack on high alkali glasses results primarily from the formation and solution of acid phosphates,[390] but in many cases a film of phosphate is formed which renders them more resistant to attack than low alkali glasses. Quartz is more resistant than either.[391]

The solubility of amorphous silica in orthophosphoric acid has been studied at 50° and 90°C.[287] At 90°C. a solid phase of variable composition, $n SiO_2, m P_2O_5, q H_2O$, is observed. The solubility of silica decreases as the concentration of the acid rises and increases with rising temperature. Equilibrium compositions in the ternary system, after 6 to 12 days at 90°C., are given in Table XLIV.

*Table XLIV.—Compositions in the Ternary System* $P_2O_5$–$SiO_2$–$H_2O$ *at* 90°C.

| Liquid phase | | Solid phase | |
|---|---|---|---|
| % $P_2O_5$ | % $SiO_2$ | % $P_2O_5$ | % $SiO_2$ |
| 4·68 | 0·029 | 3·89 | 27·30 |
| 6·98 | 0·027 | 7·60 | 32·13 |
| 13·51 | 0·019 | 9·20 | 31·53 |
| 17·74 | 0·013 | 12·89 | 29·90 |
| 26·42 | 0·006 | 20·61 | 30·84 |
| 27·52 | 0·007 | 21·90 | 26·37 |
| 42·10 | — | 33·95 | 26·41 |
| 42·14 | — | 36·47 | 25·40 |

The ternary solid phases decompose to give crystalline silicophosphates when heated to 325°–350°C. The existence of the two compounds $P_2O_5,SiO_2$ and $2P_2O_5,3SiO_2$ has been deduced from thermal, chemical, optical and *X*-ray studies of the phases separating from melts in the $P_2O_5$–$SiO_2$ system in the range 50–100 mole-% of $SiO_2$, at high temperatures and atmospheric pressure[288]; however it has also been claimed[289] that the only two crystalline phases to appear in sealed tubes at such temperatures are $P_2O_5,SiO_2$ and $P_2O_5,2SiO_2$, previous reports of $2P_2O_5,3SiO_2$ being attributed to loss of $P_2O_5$ from $P_2O_5,SiO_2$ when working in an open system at high temperature. Two modifications of $P_2O_5,SiO_2$ are reported[289]:

(*a*) a low temperature (< 700°C.) form, of which the *X*-ray powder diffraction pattern resembles closely that of the neutral silicon pyrophosphate prepared from colloidal silica solution at low temperature[285];

(*b*) a high temperature (> 1030°C.) form, with an *X*-ray powder diffraction pattern which, although similar to that of the high temperature variety,[286] differs from that of the sample prepared at high temperature from colloidal silica.[285]

It appears, therefore, that there may be at least three different crystalline modifications of $SiP_2O_7$. This is supported by an infra-red study of the system which also disclosed three isomers. Products formed at 300–350° had a loose structure and were slowly decomposed by water. Those formed at 400°–700° were dense, stable to water or $HF/H_2SO_4$, and had a lower ion exchange capacity towards Na(I) or $(UO_2)$(II) ions.[392]

The kinetics of the solution of germanium dioxide in 6–8 M. $H_3PO_4$ are most interesting. The reaction velocity increases to a maximum over 1–2 days and then declines to a very low value. The second stage is associated with the formation of $GeO_2,P_2O_5,2H_2O$, which probably has the structure $H_2[Ge(PO_4)_2],nH_2O$.[393]

### REACTION WITH BORON TRIFLUORIDE

As it does with all inorganic oxyacids, boron trifluoride forms co-ordination compounds with orthophosphoric acid, solutions of which, saturated with boron trifluoride, are widely used as catalysts in alkylation, polymerization and other organic reactions.[290]

In 1947 it was reported[291-3] that definite co-ordination compounds are formed, for example $H_3PO_4,BF_3$ and $H_4P_2O_7,2BF_3$, which are comparatively stable liquids on storage and not decomposed at 100°C. Because the compounds are difficult to purify by fractional crystallization or distillation, their physical constants are not known with any accuracy. The adducts decompose when distilled, and the orthophosphoric acid complex solidifies to a glassy mass at $-100$°C.

However, when stoicheiometrically accurate (1 in $10^4$) proportions of boron trifluoride are absorbed in orthophosphoric or deuterophosphoric acid, the 1 : 1 complexes formed have the properties shown in Table XLV.[4]

*Table XLV.—Densities, Viscosities and Electrical Conductivities of* $BF_3,H_3PO_4$ *and* $BF_3,D_3PO_4$

| | Density, $d_4^{t°}$ g./cm.$^3$ | | Viscosity, $\eta$ centipoises | | Specific conductivity, $K$ ohm$^{-1}$ cm.$^{-1}$ | |
|---|---|---|---|---|---|---|
| °C. | $BF_3,H_3PO_4$ | $BF_3,D_3PO_4$ | $BF_3,H_3PO_4$ | $BF_3,D_3PO_4$ | $BF_3,H_3PO_4$ | $BF_3,D_3PO_4$ |
| 25 | 1·8831 | 1·9058 | 46·16 | 48·51 | $8{\cdot}23 \times 10^{-3}$ | $8{\cdot}20 \times 10^{-3}$ |
| 30 | 1·8777 | 1·8990 | 39·27 | 41·66 | $9{\cdot}29 \times 10^{-3}$ | $9{\cdot}25 \times 10^{-3}$ |
| 35 | 1·8734 | 1·8933 | 34·26 | 35·85 | $10{\cdot}41 \times 10^{-3}$ | $10{\cdot}37 \times 10^{-3}$ |
| 40 | 1·8681 | 1·8870 | 30·35 | 31·11 | $11{\cdot}85 \times 10^{-3}$ | $11{\cdot}50 \times 10^{-3}$ |

Previously reported values for density and electrical conductivity of the boron trifluoride–orthophosphoric acid complex[294-6] differ from those quoted in Table XLV, and probably refer to solutions more concentrated with respect to boron trifluoride than corresponds to the mole ratio of unity. At 40°C. it was observed that one mole of orthophosphoric acid could absorb 1·084 moles of boron trifluoride.[4]

The 1 : 1 complexes of boron trifluoride and orthophosphoric or deuterophosphoric acid are very much more mobile than their parent acids and in this respect are unique among the boron trifluoride adducts. Their electrical conductivities are also much lower than those of the acids, which themselves have abnormally large conductivity. This may be attributed[4] to boron trifluoride molecules occupying sites formerly available for hydrogen bonding, which confers high viscosity and is a pre-requisite for electrical conduction by proton-jumps (see page 692). Conduction in the complexes thus proceeds by normal ionic migration. A comparison of the viscosity and conductivity of the $BF_3$ complexes of orthophosphoric and deuterophosphoric acid is given in Table XLVI.[4]

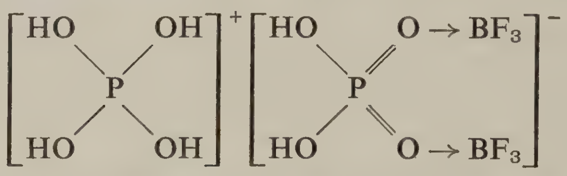
*Table XLVI.—Comparison of Viscosity and Conductivity of the* $BF_3$ *Complexes of Orthophosphoric Acid and Deuterophosphoric Acids at* 25°C.

| | $H_3PO_4$ | $BF_3,H_3PO_4$ | $D_3PO_4$ | $BF_3,D_3PO_4$ |
|---|---|---|---|---|
| Viscosity $\eta_{25}$ cps. | 177·5 | 46·16 | 231·8 | 48·51 |
| Specific conductivity $K$,ohm$^{-1}$ cm.$^{-1}$ | $4{\cdot}675 \times 10^{-2}$ | $0{\cdot}823 \times 10^{-2}$ | $2{\cdot}818 \times 10^{-2}$ | $0{\cdot}820 \times 10^{-2}$ |

Although boron trifluoride–orthophosphoric acid has been represented[297] as:

$$[H^+]_3[PO_4BF_3]^{3-}$$

on the basis of stoicheiometry, cryoscopic molecular weight determinations[294] and electrical conduction characteristics, the following structure appears more likely[4]:



Calculations show that this molten complex is ionized to the extent of about 60–70%.

A compound with half the amount of boron trifluoride, $BF_3,2H_3PO_4$, has been envisaged and some evidence exists to support this idea from a slight irregularity in the 40°C. conductivity–composition isotherm at the mole ratio 0·5.[4]

## USES OF ORTHOPHOSPHORIC ACID

By far the greatest consumption of pure orthophosphoric acid is in the preparation of various salts for use in the food, detergent and dentifrice industries, and of the less pure acid in the production of phosphatic fertilizers and detergent phosphates.

Because pure orthophosphoric acid is devoid of odour and, when greatly diluted, not injurious to health, it is often used as a constituent of tonic medicines and soft drinks. Being non-toxic it is employed for the manufacture of certain foodstuffs, such as gelatin, for removing milk-stone from dairy equipment and in the preparation of activated carbon for sugar-refining. It is also an acceptable source of supplemental phosphorus for beef cattle.

The acid is also used to control hydrogen ion concentration in the production of antibiotic drugs and often as a food for micro-organisms themselves; another application in the field of medicine is the manufacture of dental cements.

In conjunction with certain of its salts it is the basis of many preparations for metal finishing processes designed to provide protective phosphate coatings on iron, steel and other metals and the acid can also be used in pickling to remove mill-scale and rust. Orthophosphoric acid is also a constituent of solutions employed for chemically polishing brass and aluminium ware, and in the electropolishing of many metals and alloys.

In the textile industry it provides a convenient means of adjusting the acidity of the dye-bath, having no corrosive action on machinery.

Miscellaneous uses are as a coagulant in the processing of rubber latex, the production of non-corrosive soldering fluxes of the aniline phosphate type and in the preparation of dehydration, polymerization and alkylation catalysts for the oil-refining industry. The acid has also been used, in admixture with other materials, to improve the compressive strengths of clay soils.

The uses of orthophosphoric acid have been fully described, with extensive bibliographies.[298–300]

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### SECTION XXVI

# LINEAR POLYPHOSPHORIC ACIDS

BY J. E. SUCH

THE conception of a series of polyphosphoric acids derived from orthophosphoric acid by the abstraction of water, advanced as long ago as 1845 by Fleitmann and Henneberg,[1] suggested the following compounds:

| | | |
|---|---|---|
| orthophosphoric acid | $H_3PO_4$ | |
| di- or pyrophosphoric acid | $H_4P_2O_7$ | ($2H_3PO_4$ less $H_2O$) |
| triphosphoric acid | $H_5P_3O_{10}$ | ($3H_3PO_4$ less $2H_2O$) |
| tetraphosphoric acid | $H_6P_4O_{13}$ | ($4H_3PO_4$ less $3H_2O$) |
| | etc. | etc., |

the general equation for the series being

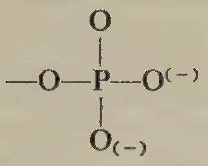
$$nH_3PO_4 = H_{n+2}P_nO_{3n+1} + (n-1)H_2O$$

When $n$ is a very large number the formula for the acid approaches $(HPO_3)_n$, which, analytically, would be indistinguishable from the last group of the three acids, originally classified by Graham as orthophosphoric, pyrophosphoric and metaphosphoric acids.

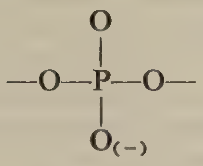
Although the salts of some of these acids, other than ortho- and pyrophosphoric acids, have been described by early workers,[2] the question of the existence of polyphosphates of acids intermediate between pyrophosphoric and so-called metaphosphoric acid remained in some doubt for nearly a century. Owing to inadequate analytical procedures and lack of knowledge of the structural arrangements of the compounds under study, it often proved difficult to decide whether many were individual bodies or just mixtures of the two end-members of the polyphosphoric acid series.

However, the application of *X*-ray, infra-red and nuclear magnetic resonance techniques has, of late years, clarified the structural problems, and the use of physico-chemical methods of analysis, such as paper and ion-exchange chromatography, permits the identification and fairly accurate determination of the various species of phosphates, either in the pure state or in mixtures. Also, since the polyphosphoric acids and their salts behave as poly-electrolytes, many of the physical methods of investigation used in the field of high polymer chemistry have, during the last two decades, been applied to them, with important results. These include the determination of molecular size by ultra-centrifugation[3-8] and diffusion,[9] end-group titration,[10] intrinsic viscosity in salt solutions,[11] cryoscopy,[12] light-scattering[13] and limiting viscosity in water[11,13,114]; the investigation of molecular shape by nuclear magnetic resonance peaks,[15-6] by flow bi-refringence[17] and anisotropy in electrical conductivity measurements[18-9] and of the size distribution of the species present in mixtures, by solubility fractionation,[20] paper-chromatography[21-2] and anion-exchange.[23-7]

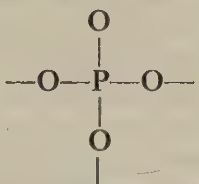
The conclusions to be drawn from these diverse fields of investigation have been reviewed,[28,146,160] and support the idea that phosphates can be regarded as phosphorus compounds with anions in which each phosphorus atom is surrounded by four oxygen atoms, tetrahedrally arranged. This is the unit for more complex structures in which, by sharing oxygen atoms between adjacent tetrahedra, chain, ring and branched polymers may be formed. Thus, it has been suggested[29] that there are three main structural units from which polyphosphates can be assembled, end groups, middle groups and branching points, which may be represented as follows:


$-O-\overset{\overset{O}{|}}{\underset{\underset{O_{(-)}}{|}}{P}}-O^{(-)}$

end group


$-O-\overset{\overset{O}{|}}{\underset{\underset{O_{(-)}}{|}}{P}}-O-$

middle group


$-O-\overset{\overset{O}{|}}{\underset{\underset{\underset{|}{O}}{|}}{P}}-O-$

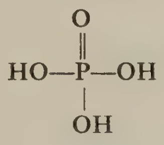
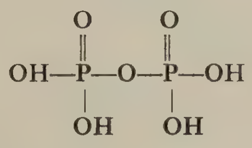
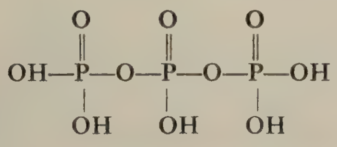
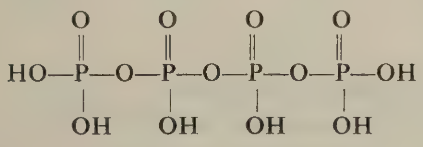
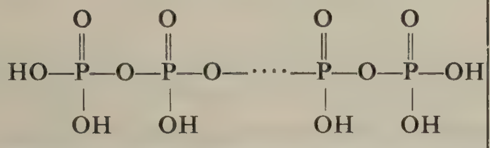
branching point

In the end $PO_4$ group, one oxygen is shared and there are two negative charges (or ester linkages); in the middle $PO_4$ group, two oxygen atoms are shared with adjacent groups and there is one negative charge (or ester linkage); finally, there is the branching point, in which three oxygen atoms are shared by neighbouring $PO_4$ groups.

By assembling two end-groups, the pyrophosphate molecule is formed, and by the addition of middle groups the series of linear polyphosphate ions can be envisaged. Combination of middle groups gives ring molecule ions and branching points can be introduced to form branched chains, or to attach rings to chains (see page 754).

The constitution of the linear polyphosphoric acids of general formula $H_{n+2}P_nO_{3n+1}$ can be depicted as shown in Table I.[30]

*Table I.—The Linear Polyphosphoric Acids of General Formula* $H_{n+2}P_nO_{3n+1}$

| Formula | % $P_2O_5$ | Constitution of acid $H_{n+2}P_nO_{3n+1}$ | Rational name | Number of dissociated hydrogen atoms | |
|---|---|---|---|---|---|
| | | | | Strong | Weak |
| $H_3PO_4$ | 72·39 |  $HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$ | mono- (ortho) | 1 | 2 |
| $H_4P_2O_7$ | 79·72 |  $OH-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$ | di- (pyro) | 2 | 2 |
| $H_5P_3O_{10}$ | 82·52 |  $OH-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$ | tri- (tripoly) | 3 | 2 |
| $H_6P_4O_{13}$ | 83·98 |  $HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$ | tetra- | 4 | 2 |
| $H_{n+2}P_nO_{3n+1}$ | — |  $HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\cdots-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$ | polyphosphoric acid | $n$ | 2 |

Although it had been suggested that phosphoric acids having a phosphoric oxide content greater than that of $H_3PO_4$ contained various polyphosphoric acids,[31-2] most early workers assumed them to be simple mixtures of orthophosphoric, pyrophosphoric and metaphosphoric acids. However, subsequent studies of the composition of such acids,[33-5] and more particularly those in which paper,[36-7] thin layer[161-2] and ion-exchange[38-40, 163] chromatography have been employed, support the conclusion that the so-called strong (or condensed) phosphoric acids are equilibrium mixtures of the various linear polyphosphoric acids, the structures of which are given in Table I, at least for compositions up to about 86% of phosphoric oxide.

It has also been established that the equilibrium composition, expressed in terms of the linear polymers, is a function of the phosphoric oxide concentration and is not dependent on the method of preparation. Equilibrium conditions, attained fairly quickly at the temperatures commonly used in the preparative methods,[41] are frozen by chilling to room temperature, at which any further rearrangements are too slow to be significant for practical purposes.

Mixtures having more than 86% of phosphoric oxide contain some cyclic polyphosphoric acids, in addition to the linear polymers,[40] but a conclusion drawn from early paper-chromatographic analyses[36] that the lower members of the polyphosphoric acid series (up to nonaphosphoric acid) tended towards zero at 88·7% $P_2O_5$, a composition equivalent to $(HPO_3)_n$, could not be substantiated from the results of later ion-exchange studies.[40] These indicated the presence, not only of linear and cyclic polyphosphoric acids in such a composition, but also of more complex ring-containing structures as well.

The compositions of phosphoric acids, in terms of the constituent polyphosphoric acids, given in Table II and in Fig. 1, are based on data contained in reference 40.

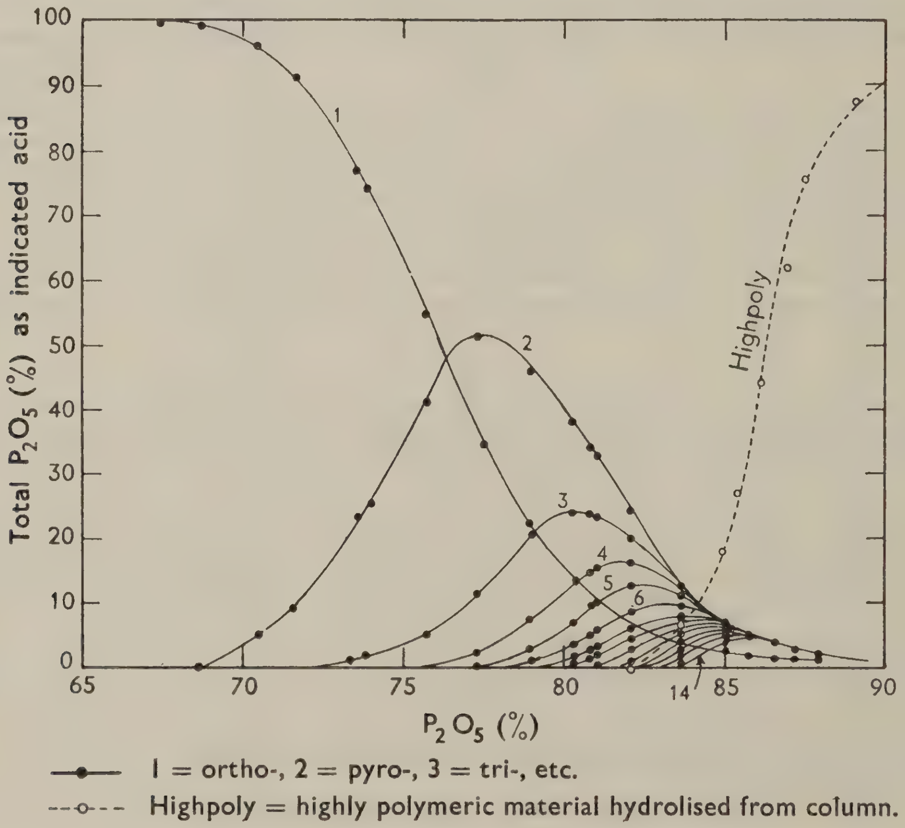


FIG. 1.—The composition of phosphoric acids

Using a flexible chain to represent the polyphosphoric acids existing in equilibrium in liquid phosphoric acids, Parks and Van Wazer[42] have calculated, from theoretical considerations, the distribution of the various species of polyphosphoric acids in liquids with varying phosphoric oxide contents. Their results are in close agreement

*Table II.—Composition of Phosphoric Acids (% Total $P_2O_5$ as Constituent Polyphosphoric Acids)*

| * | Total $P_2O_5$ % | $\frac{[P_2O_5]}{[H_2O]}$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | High-poly | Tri-meta- | Tetra-meta |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *a* | 67·4 | 0·263 | 100·0 | | | | | | | | | | | | | | | | |
| *a* | 68·7 | 0·279 | 99·7 | 0·33 | | | | | | | | | | | | | | | |
| *a* | 70·4 | 0·302 | 96·2 | 3·85 | | | | | | | | | | | | | | | |
| *a* | 71·7 | 0·321 | 91·0 | 8·86 | tr. | | | | | | | | | | | | | | |
| *a* | 73·5 | 0·352 | 77·1 | 22·1 | 0·79 | | | | | | | | | | | | | | |
| *b* | 73·9 | 0·360 | 73·6 | 25·1 | 1·34 | | | | | | | | | | | | | | |
| *b* | 75·7 | 0·394 | 53·9 | 40·7 | 4·86 | 0·46 | | | | | | | | | | | | | |
| *a* | 77·5 | 0·438 | 33·5 | 50·6 | 11·5 | 2·68 | 0·74 | tr. | | | | | | | | | | | |
| *a* | 79·1 | 0·481 | 22·1 | 46·3 | 20·3 | 7·82 | 2·26 | 1·02 | 0·34 | | | | | | | | | | |
| *b* | 80·5 | 0·523 | 13·8 | 38·2 | 23·0 | 13·0 | 6·86 | 3·38 | 1·67 | 1·03 | 0·22 | | | | | | | | |
| *b* | 81·0 | 0·542 | 12·2 | 34·0 | 22·7 | 14·6 | 8·42 | 4·36 | 2·27 | 1·41 | 0·56 | tr. | | | | | | | |
| *b* | 81·2 | 0·549 | 10·9 | 32·9 | 22·3 | 15·0 | 9·36 | 5·41 | 2·85 | 1·75 | 0·97 | 0·36 | 0·05 | | | | | | |
| *a* | 82·4 | 0·594 | 7·32 | 23·0 | 19·3 | 15·9 | 12·3 | 8·21 | 5·73 | 3·89 | 2·52 | 1·36 | 0·91 | 0·14 | | | tr. | | |
| *a* | 84·0 | 0·667 | 3·92 | 11·8 | 12·7 | 12·0 | 10·5 | 8·97 | 7·99 | 6·62 | 5·63 | 4·54 | 3·72 | 3·03 | 2·46 | 1·68 | 6·63 | | |
| *b* | 85·0 | 0·717 | 2·28 | 6·36 | 7·32 | 8·01 | 8·17 | 7·67 | 7·22 | 6·93 | 6·42 | 5·89 | 5·27 | 4·69 | 3·99 | 3·83 | 16·9 | | |
| *a* | 85·3 | 0·736 | 1·87 | 4·73 | 6·33 | 6·58 | 6·66 | 6·71 | 6·36 | 6·11 | 5·88 | 5·46 | 5·07 | 4·90 | 4·64 | 4·38 | 25·6 | | |
| *b* | 86·1 | 0·787 | 1·46 | 2·81 | 3·74 | 4·43 | 4·52 | 4·77 | 4·79 | 4·93 | 4·67 | 4·54 | 4·67 | 4·63 | 4·38 | 4·17 | 43·5 | 0·17 | |
| *b* | 87·1 | 0·860 | 0·83 | 1·81 | 2·17 | 2·53 | 3·09 | 3·39 | 3·46 | 3·33 | 3·55 | 3·47 | 3·45 | 3·52 | 3·26 | 3·24 | 61·1 | tr. | |
| *b* | 87·9 | 0·920 | 0·50 | 0·82 | 1·56 | 1·76 | 1·72 | 2·03 | 2·13 | 2·26 | 2·07 | 2·26 | 2·06 | 2·20 | 1·99 | 2·30 | 76·4 | 0·42 | 0·11 |
| *b* | 89·4 | 1·066 | 1·88 | 1·52 | 0·7 | 0·61 | 0·62 | 0·68 | 0·54 | 0·71 | 0·36 | 1·03 | 0·98 | 1·16 | 1·23 | 1·37 | 86·8 | 1·17 | 0·41 |

* *a* = prepared by dehydration of orthophosphoric acid,
*b* = prepared by dissolving phosphoric oxide in orthophosphoric acid,
1 = ortho, 2 = pyro, 3 = tri, 4 = tetra, etc.,
High-poly = material retained by resin.

with the analytical evidence so far available, except for mixtures containing more complex structures than the purely linear polyphosphoric acids upon which the theoretical calculations were based. In subsequent statistical treatments it was claimed that the amount of free orthophosphoric acid in polyphosphoric acid could be explained by regarding this acid as the fundamental unit from which the polyphosphoric acids are constructed.[152,164] A modification of these calculations, using a few empirical parameters, permitted the calculation of chain-length distributions for polyphosphoric acids which fit available data even more closely.[165] It has been observed, however, that in polyphosphoric acid obtained by dehydrating gypsum process phosphoric acid (see page 77), the distribution of polyphosphate species is displaced towards higher molecular weights, compared with pure polyphosphoric acid of the same $P_2O_5$ content.[166-7]

The rotational isomeric state theory of linear macromolecules[168] has been used to analyze the unperturbed dimensions of the polyphosphate chain. The results are explicable on the assumption that electrostatic or steric interactions cause little hindrance to rotation about one bond of the chain while all its neighbours are *trans*, but greatly impede simultaneous large rotations about pairs of adjoining bonds.[169]

### Preparation of Linear Polyphosphoric Acids

The linear polyphosphoric acids can be most readily prepared by evaporating orthophosphoric acid,[36-8,166,170] or by the addition of phosphoric oxide, (H) form, to it.[36,40,171]

The evaporation can be performed in pyrex containers up to about 180°C.,[37] in graphite crucibles up to about 350°C., at which point some reduction to elemental phosphorus begins to take place, or up to 750°C. preferably in Hastelloy, gold or platinum.[36-7,43] Evaporation in gold or platinum gives acids with stable purple or brown colours, possibly a colloidal effect.[44] Heat for the dehydration[166] or distillation[171] of phosphoric acid can be provided by burning a suitable fuel in a flame which is submerged in the acid.

When phosphoric oxide is used with orthophosphoric acid to prepare the linear polyphosphoric acids, it is often necessary to heat the mixtures as the oxide is slow to dissolve in the viscous medium. One method of doing this is to seal orthophosphoric acid and phosphoric oxide in pyrex containers and heat in a furnace, at about 350°C., for 10–20 min. and then chill rapidly to room temperature.[36]

If monoammonium phosphate is heated for 3 hours at 340°C. it loses all its ammonia and some water, giving pyrophosphoric acid. At 440°C. higher polyphosphoric acids are formed and at 600°C. branched ultraphosphoric acids result.[153]

Polyphosphoric acids are also formed in reactions between orthophosphoric acid and phosphorus oxychloride[37,45,46] of the type:

$$(n-1)\mathrm{POCl_3}+(2n+1)\mathrm{H_3PO_4} = 3\mathrm{H}_{n+2}\mathrm{P}_n\mathrm{O}_{3n+1}+3(n-1)\mathrm{HCl}$$

and it has also been claimed[47] that electrolysis of acids containing at least 72·4% $P_2O_5$, using high current density, produces polyphosphoric acids ($n=3{\cdot}5$ average) without significant formation of reduced phosphorus compounds. The reaction of phosphoric oxide with hydrogen peroxide yields permonophosphoric acid and the lower polyphosphoric acids. No tetrametaphosphoric acid is detected, since the lower cyclic phosphoric acids are rapidly decomposed by water in presence of excess hydrogen peroxide.[172] Tetraphosphorus hendecaoxide, $P_4O_{11}$, is said to yield a mixture of perdiphosphoric and pyrophosphoric acids on treatment with water.[173] The lower polyphosphoric acids and their esters have also been detected in the so-called 'Langheld ester', obtained by the reaction of phosphoric oxide with diethyl ether.[174]

### Physical Properties of Linear Polyphosphoric Acids

The linear polyphosphoric acids are very hygroscopic and range, at room temperature, from viscous liquids through gums to glassy solids when containing more than 86% $P_2O_5$.[37] The only known crystalline compositions in the phosphoric oxide–water system, apart from orthophosphoric acid hemi-hydrate, $4H_2O,P_2O_5$, and orthophosphoric acid itself, $3H_2O,P_2O_5$, are the two forms of pyrophosphoric acid (q.v.). A crystalline tetraphosphoric acid, $3H_2O,2P_2O_5$, has been reported,[48–9] but it is more than likely that this was actually one of the two crystalline forms of pyrophosphoric acid, produced either by surface hydrolysis or slow crystallization from the liquid acid[37]; there is also some doubt about the identity of a crystalline metaphosphoric acid, $H_2O,P_2O_5$, described in the literature.[50–1]

### DENSITY

The densities of acids with phosphoric oxide contents in the range 72·43–88·74% $P_2O_5$, which are given in Table III, have been extracted from data published by the Tennessee Valley Authority.[52]

*Table III.—Density of Linear Polyphosphoric Acids*

| Concentration wt.-% $P_2O_5$ | Density, g./c.c. at indicated temperature, °C. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 25 | 30 | 40 | 50 | 75 | 100 | 125 | 150 |
| 72·43 | 1·863 | 1·859 | 1·852 | 1·845 | 1·826 | 1·808 | 1·789 | 1·771 |
| 74 | 1·889 | 1·885 | 1·878 | 1·871 | 1·852 | 1·834 | 1·816 | 1·798 |
| 76 | 1·921 | 1·918 | 1·911 | 1·903 | 1·886 | 1·868 | 1·850 | 1·832 |
| 78 | 1·954 | 1·950 | 1·943 | 1·936 | 1·919 | 1·901 | 1·884 | 1·866 |
| 79·76 | 1·983 | 1·979 | 1·972 | 1·965 | 1·948 | 1·931 | 1·914 | 1·896 |
| 80 | 1·987 | 1·983 | 1·976 | 1·969 | 1·952 | 1·935 | 1·918 | 1·900 |
| 82 | 2·019 | 2·016 | 2·009 | 2·002 | 1·985 | 1·968 | 1·951 | 1·934 |
| 84 | 2·052 | 2·049 | 2·042 | 2·035 | 2·019 | 2·002 | 1·985 | 1·969 |
| 86 | 2·084 | 2·081 | 2·075 | 2·068 | 2·052 | 2·035 | 2·019 | 2·003 |
| 88·74 | 2·129 | 2·126 | 2·120 | 2·113 | 2·097 | 2·081 | 2·065 | 2·049 |

*Table IV.—Kinematic Viscosity in Centistokes of Polyphosphoric Acids, 72·43–85·41% $P_2O_5$*

| °C. | % $P_2O_5$ | | | | |
|---|---|---|---|---|---|
| | 72·43 | 76·01 | 79·63 | 83·25 | 85·41 |
| 20 | 140 | 600 | — | — | — |
| 25 | 100 | 440 | 2200 | — | — |
| 30 | 81 | 330 | 1600 | — | — |
| 40 | 53 | 173 | 810 | — | — |
| 50 | 36 | 110 | 410 | — | — |
| 60 | 25 | 70 | 270 | 1500 | — |
| 70 | 19 | 50 | 170 | 1000 | — |
| 80 | 14 | 33 | 100 | 600 | 2000 |
| 90 | 11 | 25 | 67 | 380 | 1200 |
| 100 | 9·2 | 19 | 50 | 250 | 830 |
| 110 | 7·7 | 15 | 38 | 190 | 550 |
| 120 | 6·2 | 12 | 29 | 120 | 400 |
| 130 | 5·2 | 9·6 | 22 | 99 | 320 |
| 140 | 4·5 | 8·0 | 18 | 68 | 210 |
| 150 | 4·1 | 7·1 | 15 | 54 | 170 |
| 160 | 3·5 | 6·0 | 13 | 41 | 130 |
| 170 | 3·2 | 5·2 | 10 | 34 | 107 |
| 180 | 2·9 | 4·5 | 8·8 | 28 | 87 |

To a first approximation, the densities of the polyphosphoric acids are proportional to their phosphoric oxide contents and the following equation, although not in exact conformity with the data in Table III, is relevant:

$$d_{25^\circ\text{C.}} = 0{\cdot}0167 \times (\%\ P_2O_5) + 0{\cdot}66 \quad \text{for} \quad 50 < \%\ P_2O_5 < 95$$

and the temperature correction:

$$d_{t^\circ\text{C.}} = d_{25^\circ\text{C.}} - 0{\cdot}0009(t^\circ\text{C.} - 25)$$

may be applied.[51]

VISCOSITY

The kinematic viscosity, in centistokes, of certain polyphosphoric acids at the indicated temperatures is shown in Table IV, the accuracy claimed being of the order of 10%.[52]

Other, possibly more accurate, data obtained by the Hoeppler rolling-ball viscometer for a narrower range of compositions, and at temperatures for which values were not given in Table IV, are shown in Table V.[53]

*Table V.—Dynamic Viscosity in Centipoises of Polyphosphoric Acids,* 81·47–84·39% $P_2O_5$

| $t$°C. ± 0·01°C. | % $P_2O_5$ | | | | |
|---|---|---|---|---|---|
| | 81·47 | 81·57 | 82·44 | 83·57 | 84·39 |
| 24·92 | 21,672 | — | — | — | — |
| 34·37 | 8,740 | — | — | — | — |
| 39·32 | 5,995 | — | — | — | — |
| 44·42 | 4,170 | — | 6891 | 13,506 | 27,616 |
| 49·47 | — | 3003 | 4885 | 9,227 | 19,726 |
| 54·62 | — | 2339 | 3780 | 6,639 | 16,774 |

Fig. 2 (reference 51) shows the variation of viscosity with temperature for a wide range of polyphosphoric acids. Those with more than 86·4% of phosphoric oxide probably contain branched (q.v.) in addition to linear polymers, and their viscosities were derived from the data[54] given in Table VI.

*Table VI.—Variation of Viscosity of Polyphosphoric Acid with Temperature, according to the Equation* $\eta$ *poises* $= ae^{(E_{\text{vis.}}/RT)}$

| $H_2O/P_2O_5$ mole ratio | % $P_2O_5$ | Temperature range °C. | $a$ (× $10^3$) | $E_{\text{vis.}}$ kcal. |
|---|---|---|---|---|
| 0·60 | 92·9 | 400–600 | 1·825 | 17·502 |
| 0·68 | 92·1 | 375–600 | 3·076 | 14·689 |
| 0·88 | 92·0 | 275–550 | 0·681 | 13·721 |
| 0·98 | 89·6 | 250–350 | 0·619 | 12·245 |
| 1·05 | 88·8 | 250–325 | 0·139 | 12·401 |
| 1·24 | 86·4 | 75–200 | 0·221 | 8·494 |

ELECTRICAL CONDUCTIVITY

The specific electrical conductivity of phosphoric acid (62·15–85·58% $P_2O_5$) has been measured at 25–60°C.[175] The results, given in Table VII, differ slightly from previous results recorded in this region, and discussed elsewhere (page 693).

*Table VII.—Specific Conductivity of Concentrated Phosphoric Acid*

| Concn., wt. % $P_2O_5$ | Specific conductivity, $ohm^{-1}$ $cm.^{-1}$ | | | | |
|---|---|---|---|---|---|
| | 25·0°C. | 30·0°C. | 40·0°C. | 50·0°C. | 60·0°C. |
| 62·14 | 0·0888 | 0·102 | 0·134 | 0·167 | 0·202 |
| 64·08 | 0·0801 | 0·0928 | 0·122 | 0·154 | 0·189 |
| 65·58 | 0·0734 | 0·0858 | 0·114 | 0·146 | 0·180 |
| 67·89 | 0·0641 | 0·0756 | 0·102 | 0·131 | 0·165 |
| 70·31 | 0·0535 | 0·0639 | 0·0870 | 0·115 | 0·145 |
| 72·25 | 0·0447 | 0·0534 | 0·0740 | 0·0975 | 0·124 |
| 73·61 | 0·0355 | 0·0432 | 0·0606 | 0·0814 | 0·106 |
| 75·64 | 0·0210 | 0·0262 | 0·0389 | 0·0550 | 0·0744 |
| 77·33 | 0·0115 | 0·0148 | 0·0234 | 0·0346 | 0·0490 |
| 80·03 | 0·00336 | 0·00471 | 0·00855 | 0·0141 | 0·0220 |
| 81·54 | 0·00175 | 0·00256 | 0·00495 | 0·00855 | 0·0137 |
| 83·77 | 0·000860 | 0·00125 | 0·00245 | 0·00429 | 0·00699 |
| 85·58 | 0·000183 | 0·000282 | 0·000597 | 0·00108 | 0·00183 |

### REFRACTIVE INDEX

The refractive index, at 25°C., of polyphosphoric acids, in the narrow range of composition 81·57–84·47% $P_2O_5$, varies linearly with concentration; it was found to be constant on storage under dry conditions and also after repeated heating and cooling cycles,[53] see Table VIII.

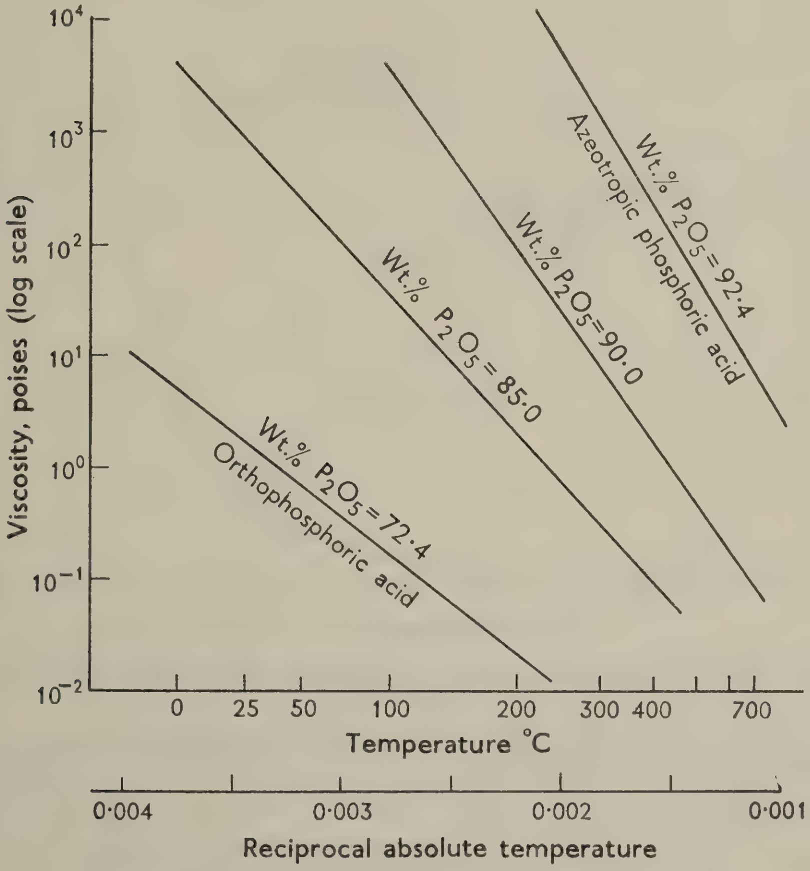


FIG. 2.—Variation of viscosity of polyphosphoric acids with temperature

### VAPOUR PRESSURE AND VAPORIZATION OF POLYPHOSPHORIC ACIDS

Vapour pressure equations and boiling points[43] have been given, for polyphosphoric acids containing 72·4–92·7% $P_2O_5$, in Table VI, Section XXV (see page 676).

These data have been used to deduce the following equation,[51] which is said to fit the data in the range 50–100 mm. to 760 mm. of Hg over the composition range 20–92% within experimental error:

$$\log_{10} p_{\text{mm}} = 8{\cdot}7788 - (5{\cdot}9080 \times \text{b.p.}/T)$$

where $p_{\text{mm}}$ is the vapour pressure in mm. Hg of the given acid at the temperature $T$ (°K.) and b.p. is the boiling point in °K. as measured at 760 mm.

*Table VIII.—Refractive Index of Polyphosphoric Acids at* 25°C.

| % $P_2O_5$ | $n_D^{25}$ |
|---|---|
| 81·57 | 1·4700 |
| 82·46 | 1·4711 |
| 83·57 | 1·4725 |
| 84·47 | 1·4735 |

The boiling points of various compositions in the $P_2O_5$–$H_2O$ system are shown in Fig. 3. The boiling point increases only slowly up to compositions containing 60–70% $P_2O_5$; thereafter the rise is rapid. The presence of an azeotrope has been demonstrated[43, 55]; when orthophosphoric acid is heated, both water and phosphoric oxide eventually volatilize until an azeotropic mixture is obtained, which varies in composition from 91·1 to 92·1% $P_2O_5$ as the pressure in the system at its boiling point increases from 104 to 753 mm., the corresponding boiling points being 694° and 869°C. respectively. The azeotropic composition can be obtained from samples both richer and poorer in phosphoric oxide. At 760 mm. the boiling point and composition of the azeotrope are about 864°C. and 92·4% $P_2O_5$.

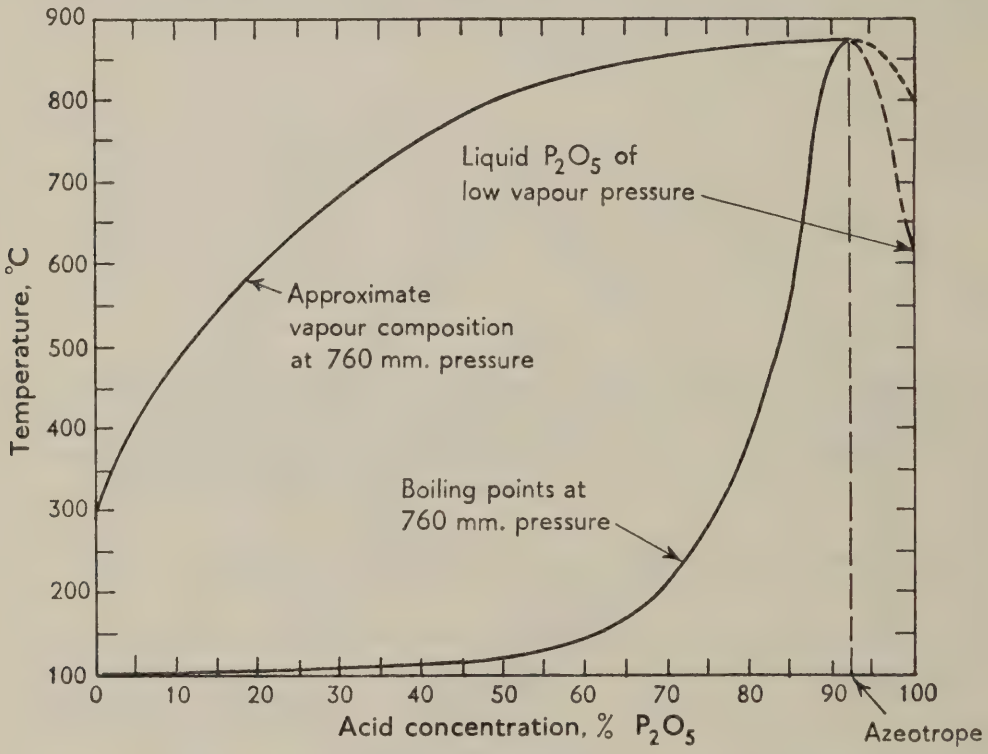


FIG. 3.—Boiling points and vapour compositions in the system $P_2O_5$–$H_2O$

The composition of the vapour above boiling phosphoric acid becomes progressively richer in phosphoric oxide up to the azeotrope, when both vapour and liquid have the same composition.[43] This change is shown graphically in Fig. 3.

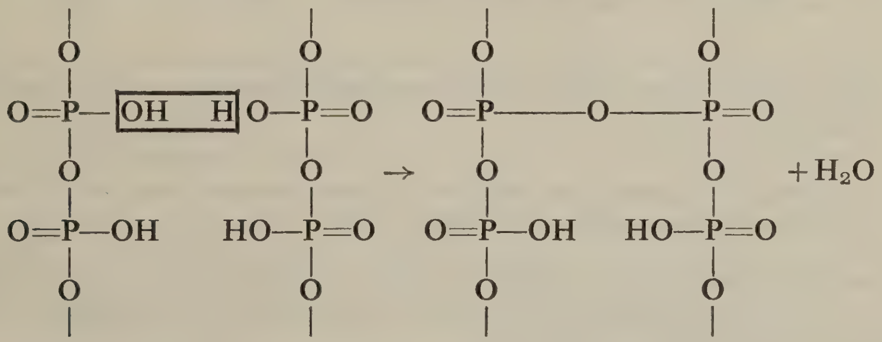
The nature of the molecular species in the vapour phase has been discussed.[51,55] Early vapour density measurements had suggested that the vapour over samples containing 91% of phosphoric oxide contained the dimeric form of so-called metaphosphoric acid, $(HPO_3)_2$; the most recent[43] vapour density determinations at 1020°C., however, indicate that the vapour consists of a mixture of water and phosphoric oxide vapour ($P_4O_{10}$) and, possibly, low molecular weight 'ultraphosphate' compounds of the type $H_2O,3P_2O_5$ (see Table IX).

*Table IX.—Apparent Molecular Weights in the* $H_2O–P_2O_5$ *System at* 1020°C.[51]

| % $P_2O_5$ in liquid | Acid composition | Mol. wt. observed | Mol. wt. calculated assuming vapour to be | |
|---|---|---|---|---|
| | | | $P_4O_{10}+H_2O$ | $H_2O,3P_2O_5+H_2O$ |
| 61·5 | 85% $H_3PO_4$ | 44·8 | 42·4 | 43·7 |
| 72·4 | 100% $H_3PO_4$ | 56·0 | 56·0 | 58·8 |
| 88·0 | Near 'meta phosphoric acid', $(HPO_3)_x$ | 109·6 | 102·4 | 107·8 |
| 92·0 | Azeotropic acid | 132·2 | 130·0 | 153·0 |

In an attempt to identify the constituents present, the vapours from phosphoric acid melts held at 450°C. (which varied in composition with heating time) were condensed by quenching in liquid air. The products were analyzed chromatographically; it was not possible to identify tetrametaphosphoric acid, which might have been expected to be present as the first identifiable hydrolysis product of phosphoric oxide, but only high molecular weight polyphosphoric acids.[37,56] It appears that there is insufficient evidence, to date, to be specific on this problem.

Acids containing more than about 92% $P_2O_5$, sometimes called ultraphosphoric acids, have not been very thoroughly studied, but it has been suggested[37] that cross-linking of long chain polyphosphoric acids can take place as follows:



leading to the formation of three-dimensional networks with the required high phosphoric oxide content, analogous in structure to some of the forms of phosphoric oxide itself (see pages 390, 391). The presence of up to 20% trimetaphosphate among the products of hydrolysis of ultraphosphates has been claimed as evidence that cyclic structures, joined in linear or two dimensional arrangements, are present in these networks.[176]

## Chemical Properties of Linear Polyphosphoric Acids

The linear polyphosphoric acids are strongly hygroscopic at room temperature and, when exposed to moist air, rapidly become less viscous and undergo hydrolysis to less complex forms; storage under strictly anhydrous conditions is therefore necessary to preserve their original composition.

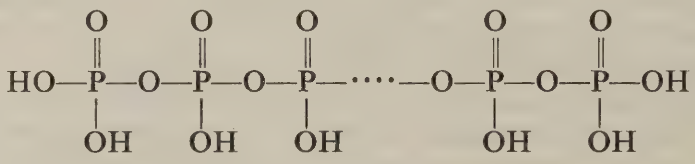
When linear polyphosphoric acids are dissolved in water, unless precautions are taken to cool the mixture, the rise in temperature on dilution causes rapid hydrolytic degradation to mixtures of less complex acids. If the conditions of dilution are accompanied by a large increase in temperature, the polyphosphoric acids present are converted almost completely to the orthophosphate state. For example, if an acid containing 84% $P_2O_5$, corresponding to tetraphosphoric acid, $H_6P_4O_{13}$, is diluted with water to approximately 54% $P_2O_5$, corresponding to 75% $H_3PO_4$, without cooling, the temperature of the solution rises to 120–140°C. and the hydrolysis to orthophosphoric acid is completed in less than 2 min.[34]

Hydrolytic degradation on dilution is reduced to a minimum if the acids are slowly added to sufficient ice-cold normal sodium or potassium hydroxide to keep the solution alkaline at all times.[37]

When stored under dry conditions, only those linear polyphosphoric acids of which the compositions correspond approximately to pyrophosphoric acid (79·72% $P_2O_5$) crystallize on long standing.[35–6, 57–60] As the solid phase usually has a different composition from the liquid phase in terms of the constituent polyphosphoric acids, such methods of investigation require careful interpretation; in addition, supercooling of the highly viscous liquids renders accurate observations of the freezing points difficult (see also under Orthophosphoric and Pyrophosphoric Acids).

NEUTRALIZATION—pH TITRATION CURVES

It has been noted[37, 61–2] that linear polyphosphoric acids contain two different kinds of hydroxyl groups which can be distinguished by their ionization constants and consequently by their behaviour on neutralization. If the linear polyphosphoric acids are presented schematically by the formulation



$$\mathrm{HO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}\cdots\cdots{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH}$$

the two types of hydroxyl groups are as follows:

(*a*) Strongly dissociated hydroxyl groups, of which there is one attached to each phosphorus atom in the chain; these may be determined by titrating with an alkali to a pH of about 4·5.

(*b*) Weakly dissociated hydroxyl groups, of which there are two, one in each of the end $PO_4$ groups in the chain; these may be determined by titration between pH about 4·5 and pH about 9·0.

If (*a*) and (*b*) represent the numbers of strong and weak acid groups, respectively, then the average chain length, $n$, of a mixture of polyphosphoric acids, in which $n$ is equal to or greater than 2, is given by:

$$n = \frac{2a}{b}$$

Since mono- (ortho) and di- (pyro) phosphoric acids both have the same ratio of strong to weakly acid groups, namely unity, corrections to the above equation must be made when calculating the average chain length of mixtures of polyphosphoric acids containing free orthophosphoric acid. If $c$ represents the number of orthophosphate phosphorus atoms present in the mixture (which can be determined by suitable alternative analytical procedures, such as colorimetry) then the corrected equation for average chain length becomes:

$$n = \frac{2(a-c)}{b-c}$$

Differential titration methods have been described for the determination of the average chain length of the linear polyphosphoric acids, which employ the principles outlined above and which can also be corrected to take into account the presence of not only orthophosphoric but cyclic and branched polyphosphoric acids as well.[10,37,63–5]

Electrometric titration curves obtained for freshly prepared solutions of various linear and cyclic polyphosphoric acids[61–2] are depicted in Fig. 4.

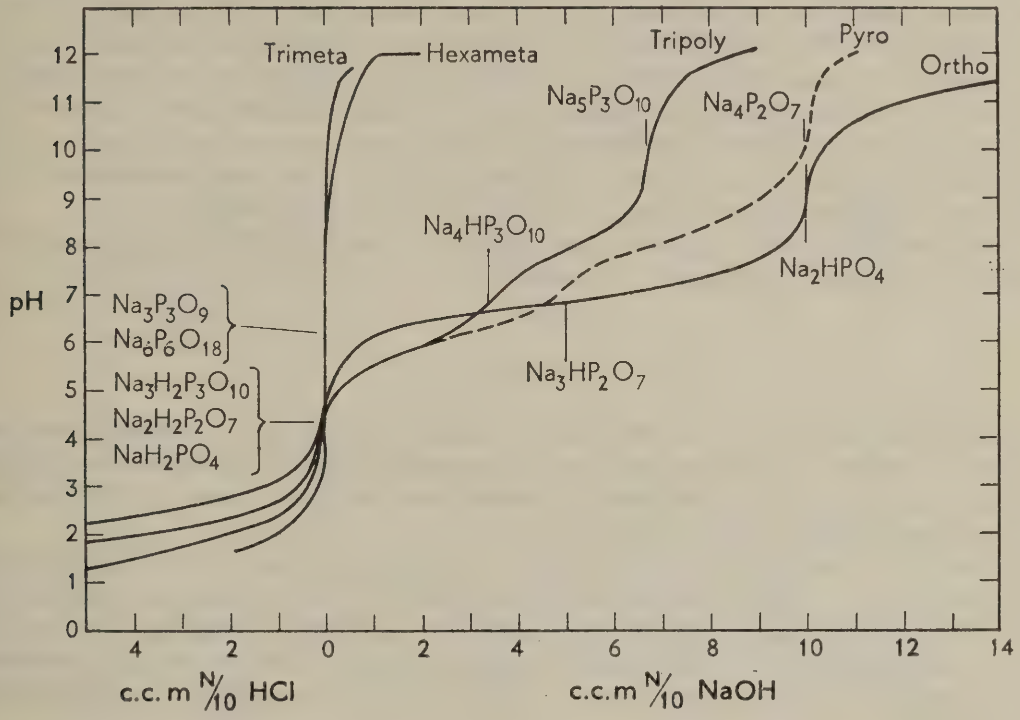


FIG. 4.—pH titration of linear and cyclic polyphosphoric acids

The main points of interest in these curves have been thoroughly discussed[51,61,66]; briefly, it has been stated that:

(i) for each phosphorus atom, in a linear polyphosphoric acid, there is one strongly dissociated hydrogen atom, $K_{\text{dissoc.}}$ approximately 10 to $10^{-3}$;
(ii) there is a weakly dissociated hydrogen atom attached to each of the phosphorus atoms at the ends of the chain, $K_{\text{dissoc.}}$ approximately $10^{-7}$ to $10^{-9}$;
(iii) strong inflection points on the titration curves occur, therefore, at pH values of about 4·5 and near to 10; the third hydrogen of orthophosphoric acid, $K_{\text{dissoc.}}$ about $10^{-13}$, is too weak to titrate;
(iv) pyrophosphoric and triphosphoric acids show three inflection points, a small change being observed near pH 7, in addition to the usual pronounced change points at pH 4·5 and 10;
(v) as the chain length of the polyphosphoric acid increases, the small middle inflection becomes less pronounced until the shape of the titration curve approaches that of the strongest of the phosphoric acids, namely the cyclic trimetaphosphoric and tetrametaphosphoric acids, and is similar to that of hydrochloric acid;
(vi) the strong acid portion of the diagram shows also that the titration curves approach the first neutralization point more gradually as the chain length increases. This behaviour is characteristic of polyelectrolytes and has been ascribed to ion-association due to electrostatic attraction.[61,66]

ACTION ON METALS

Generally speaking the corrosive action of the linear polyphosphoric acids on metals is much less than that of orthophosphoric acid itself, the effect becoming less pronounced as the concentration of phosphoric oxide increases. Aeration and the presence of impurities increase the rate of attack on most metals and at high temperature the acids are all very corrosive to both metals and ceramics, the best containers under these conditions, up to 350°C., being gold, platinum and graphite.

The corrosive action of polyphosphoric acid containing about 84% $P_2O_5$, a composition corresponding to tetraphosphoric acid, $H_6P_4O_{13}$, is slight on most metals at room temperature, the penetration of mild steel being only 0·001 in./year, rising to 0·016 in./year at 60°C. Most alloys show excellent resistance to this acid at 60°C., except nickel and lead alloys, which corrode rapidly. Plastics and rubber compositions are little affected up to this temperature. At higher temperatures, 120°–180°C., the casting alloys, such as Hastelloy and Illium, show excellent resistance, as does molybdenum-bearing stainless steel. At 240°C. this acid is very destructive to all metals and alloys and also to glass, silica being taken into solution.

Further details of the corrosive properties of polyphosphoric acids may be obtained by consulting references 34 and 67.

### Uses

Polyphosphoric acids in the composition range 76–84% $P_2O_5$ are useful reagents in organic syntheses involving inter- and intra-molecular dehydrations and in the Beckmann and Lossen rearrangements; several reviews with extensive biliographies have been compiled on this theme.[68–70,177–8]

Acids with a phosphoric oxide content near to 76% have been used in the production of fertilizers,[67] whilst those in the region of 80% $P_2O_5$, close to the composition required for pyrophosphoric acid, are useful for pickling,[71] cleaning[72] or polishing[73–6] metals and alloys; other uses for polyphosphoric acids are as high temperature lubricants[77] and in the preparation of silico-phosphate and other catalysts for the oil industry.[78–86]

The reaction products of metallic oxides and polyphosphoric acids have been suggested as bonding agents.[87]

Since the higher linear polyphosphates are precipitated under acid conditions, pH 2–4, by various dibasic amino-acids, dipeptides, guanidinium compounds and amines, such reactions may be used to separate basic biological compounds.[88]

## PYROPHOSPHORIC (OR DIPHOSPHORIC) ACID, $H_4P_2O_7$

### Preparation and Crystalline Forms

Syrupy liquids having a composition corresponding closely to pyrophosphoric acid, 79·79% $P_2O_5$, can be prepared by the evaporation of water from orthophosphoric acid or by heating it together with the required amount of phosphoric oxide. Such liquids are, however, mixtures of polyphosphoric acids, as first shown by classical[58] and later by chromatographic[36–7,40] methods of analysis. The approximate composition of liquids with phosphoric oxide contents in the pyrophosphoric acid region is shown in Table X.

Liquids containing 79–80% $P_2O_5$ do, however, crystallize on prolonged standing at or slightly below room temperature,[35,37,58,89–90] but the solid phase which is separable may not consist entirely of pyrophosphoric acid, for it has been reported[37] that orthophosphoric and other polyphosphoric acids can be identified by chromatographic analysis. The compositions of crystalline and liquid products, both containing 78·8% $P_2O_5$, are given in Table XI.

The reorganization of species is apparently reversible, for by just re-melting the crystalline solid,[92] or by tempering at more elevated temperatures,[37, 91] the composition of the cooled liquid soon reverts to that of the original mixture of polyphosphoric acids from which the solid separated.

The melting point of the hygroscopic solid crystallizing from a liquid of phosphoric oxide content corresponding to pyrophosphoric acid was first reported to be near 61°C.,[60, 89–90] but a more detailed study[59] by a slow melting technique of the phases separating from the phosphoric oxide–water system has revealed that pyrophosphoric acid can crystallize in two forms. The one usually obtained is metastable and melts at 54·3°C., the other at 71·5°C.; they can be distinguished and recognized by differences in their *X*-ray diffraction patterns.

*Table X.—Composition of Liquid Acids in the Region of Pyrophosphoric Acid*

| % $P_2O_5$ content | 79·45[36] | 79·0[37] | 79·1[40] |
|---|---|---|---|
| % total $P_2O_5$ present as | | | |
| Orthophosphoric acid | 16·7 | 29 | 22·1 |
| Pyrophosphoric acid | 43·3 | 47 | 46·3 |
| Triphosphoric acid | 22·1 | 16 | 20·3 |
| Tetraphosphoric acid | 10·7 | 6 | 7·8 |
| Pentaphosphoric acid | 4·5 | 2 | 2·3 |
| Hexaphosphoric acid | 1·9 | | 1·0 |
| Heptaphosphoric acid | 0·8 | | 0·3 |

*Table XI.—Compositions of Crystalline and Liquid Products both containing* 78·8% $P_2O_5$ [37]

| % total phosphorus present as $H_{n+2}P_nO_{3n+1}$ | | | | | |
|---|---|---|---|---|---|
| $n=$ | 1 | 2 | 3 | 4 | 5 |
| Solid state | 18·9 | 77·6 | 3·5 | nil | nil |
| Liquid state | 29·3 | 49·6 | 15·6 | 4·0 | 1·5 |

When a slurry containing the usual form, $H_4P_2O_7$–I, is heated over the range 50–54°C. without stirring, the solid melts and only a few crystals remain. With further increase in temperature the solid increases again until at 60°C. the entire mass solidifies to give the second stable form $H_4P_2O_7$–II.

The melting point diagram for the orthophosphoric–pyrophosphoric acid system based on available data[51, 59–60, 93] is shown in Fig. 5.

Beside the two forms of pyrophosphoric acid, provisionally designated $H_4P_2O_7$–I and $H_4P_2O_7$–II, a simple eutectic has been reported at 75·4% phosphoric oxide and 16°C., the lowest temperature at which a liquid phase was observed[51, 59]; the existence of reported[58] hydrated forms of pyrophosphoric acid has not been confirmed.

However, the system is far from ideal, containing several species in addition to the principal ones. The observed melting points in Fig. 5 relate to gross compositions and, in addition, it has been pointed out[59] that the values obtained depend to some extent on the thermal history of the sample being studied, to what extent the formation of solid solutions has occurred and what rearrangement of phosphate species has taken place in the liquid phase.

Dilute solutions of pure pyrophosphoric acid may best be prepared from recrystallized sodium pyrophosphate by cation exchange, or by the older method of treating aqueous suspensions of insoluble pyrophosphates, such as copper or lead, with hydrogen sulphide, filtering rapidly and aerating the well-cooled solutions to remove the excess hydrogen sulphide.[94] The evaporation of dilute aqueous solutions of pyrophosphoric acid obtained in these ways is not to be recommended on account of the risk of hydrolytic degradation to orthophosphoric acid, even at low temperatures. A laboratory method has been given for the preparation of pure crystalline pyrophosphoric acid.[179]

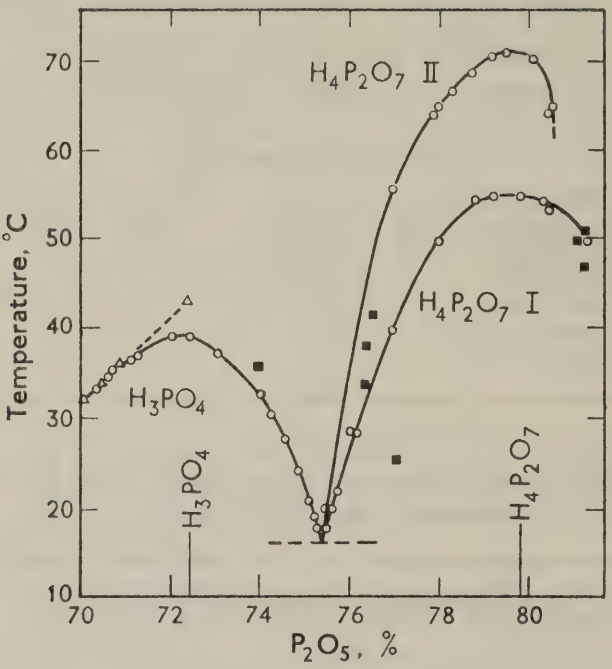


FIG. 5.—Melting point diagram for the system orthophosphoric acid-pyrophosphoric acid

△ Ross and Jones[93]
■ Bassett[60]
○ Wakefield and Egan[59]

## Physical Properties of Pyrophosphoric Acid

### THERMO-CHEMICAL DATA

Thermo-chemical data for pyrophosphoric acid are scanty and the compound has received but little attention since the original work of Giran[90]; the following values, based on his results, and quoted by the National Bureau of Standards,[95] obviously require revision in view of the most recent investigations of the phase diagram:

| | | |
|---|---|---|
| Heat of formation at 25°C., | $H_4P_2O_{7(\mathrm{crystalline})}$ | −538 kcal./mole |
| | $H_4P_2O_{7(\mathrm{liquid})}$ | −545·9 kcal./mole |
| Heat of fusion at 61°C. | | 2·2 kcal./mole |
| Entropy of fusion | | 6·587 cal./mole/°C. |

### THE DISSOCIATION OF PYROPHOSPHORIC ACID IN WATER

The ionization of pyrophosphoric acid can, most simply, be regarded as taking place in four steps:

$$\begin{aligned} H_4P_2O_7 &\rightleftharpoons H^+ + H_3P_2O_7^- \\ H_3P_2O_7^- &\rightleftharpoons H^+ + H_2P_2O_7^{2-} \\ H_2P_2O_7^{2-} &\rightleftharpoons H^+ + HP_2O_7^{3-} \\ HP_2O_7^{3-} &\rightleftharpoons H^+ + P_2O_7^{4-} \end{aligned}$$

Measurements have been made of the dissociation constants of each stage by a variety of methods and under different conditions. Values have been derived from conductivity measurements,[94,96] electrometric or complex-ion stability titrations[23,97–106,154–6,180–1] and reversion rate studies.[107–8] Owing to the wide variation of ionic strengths and temperatures employed by different authors it is not always possible to compare results on the same basis. However, in dilute solutions of ionic strength $\mu = 0{\cdot}1$ at 25°C., approximate values for the apparent dissociation constants ($K$) of the four ionization stages referred to above, and their negative logarithms (p$K$) are:

| | | | |
|---|---|---|---|
| $K_1$ | $\sim 10^{-1}$ | p$K_1$ | 1 |
| $K_2$ | $\sim 1{\cdot}5 \times 10^{-2}$ | p$K_2$ | 2 |
| $K_3$ | $2{\cdot}7 \times 10^{-7}$ | p$K_3$ | 6·57 |
| $K_4$ | $2{\cdot}4 \times 10^{-10}$ | p$K_4$ | 9·62 |

Many other values for the thermodynamic constants at infinite dilution and for apparent constants at other concentrations, in the presence of differing swamping electrolytes and at various temperatures, are contained in the references quoted. The standard free energy, enthalpy and entropy of proton dissociation have also been reported.[157,180–1]

To account for the unexpectedly rapid overall rate of reversion of pyrophosphoric to orthophosphoric acid at 60°C., in the pH range 0·38–1·79, it has been suggested[108] (see also Refs. 151, 183), that the ionic species $H_5P_2O_7^+$ is present under such conditions and that the corresponding dissociation constant, calculated from the observed reversion rate constants, is $\geqq 1 \times 10^2$.

The calculation of ionization constants on the basis of molecular structure has been applied to pyrophosphoric acid.[106,109–10] It has been claimed[106] that the application of a particular set of rules, based on considerations of molecular symmetry, gives values of p$K_1$, p$K_2$, etc., which are within 0·3 p$K$ units of those observed for polyphosphoric acids, such as pyrophosphoric and triphosphoric acids. In the same reference the theory is advanced that the wide variations in p$K$ values often obtained from titration measurements can be attributed to various ionization equilibria, other than the simple stages referred to above, which occur simultaneously in defined ranges of pH. In particular, condensation and disproportionation reactions are invoked, of the type for example,

$$2H_2P_2O_7^{2-} \leftrightarrows H_2P_4O_{13}^{4-} + H_2O \rightleftharpoons H_2P_3O_{10}^{3-} + H_2PO_4^-$$

There is some evidence to support this theory from studies of the equilibria set up in orthophosphate solutions containing phosphatase enzymes,[111–2] but later investigations in more dilute solution failed to confirm the formation of pyrophosphate from orthophosphate in the presence of homogenates of intestinal mucosa.[113] In the absence of enzymatic influence, it has been claimed,[114] however, that at equilibrium at 100°C. 100 g. of a concentrated aqueous solution of monosodium dihydrogen orthophosphate, originally 60% by weight, contained 0·16 g. of pyrophosphate, calculated as $Na_2H_2P_2O_7$.

The thermodynamic equilibrium constant for the reaction:

$$H_2P_2O_7^{2-} + H_2O \rightleftharpoons 2H_2PO_4^-$$

is reported[114] to be $0{\cdot}22 \times 10^2$ at 100°C. and $2{\cdot}2 \times 10^2$ at 25°C., from which it was deduced that detectable amounts of pyrophosphate would not be present in orthophosphate solutions less concentrated than 30–35%. The importance and role of such equilibria in biological systems has been discussed.[106,114]

The corresponding equilibrium:

$$2H_3PO_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_4P_2O_7 + H_2O$$

has been studied by an electrical conductivity method. The following thermodynamic values were obtained:

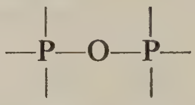
$$\begin{aligned}\Delta H^\circ &= 3{\cdot}3 \pm 1 \text{ kcal./mole}\\ \Delta F^\circ &= 1{\cdot}9 \pm 0{\cdot}2 \text{ kcal./mole}\\ \Delta S^\circ &= +4 \text{ e.u. at } 0\text{–}100^\circ\end{aligned}$$

The activation energy associated with $k_1$ is found to be $20 \pm 1$ kcal., and with $k_2$ 17 kcal./mole.[182]

A method has been developed for calculating the concentration of the ionic species present in pyrophosphoric acid solutions of differing hydrogen ion concentration, using selected values for the dissociation constants of each ionization stage.[115]

### THE HYDROLYTIC DEGRADATION OF PYROPHOSPHORIC ACID

In aqueous solution all linear and cyclic polyphosphoric acids and their salts hydrolyze at their

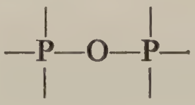


$$-\overset{|}{\underset{|}{\mathrm{P}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{P}}}-$$

linkages, being ultimately degraded to the thermodynamically stable orthophosphate ion. In respect of hydrolytic degradation they are similar to other polyacids, but differ from polysulphates, polyborates and possibly polysilicates inasmuch as instead of hydrolyzing almost as fast as solution occurs, their stability is very much greater. The half-life of the above linkage at room temperature, at neutral pH and in 1% aqueous solution is of the order of magnitude of years.

The hydrolytic breakdown of polyphosphates has been widely studied in order to ascertain the kinetics and mechanism of the processes involved and to assess the practical utility of aqueous solutions, since their ability to form soluble complexes with di- and tri-valent cations diminishes on hydrolysis, because the final reversion product does not possess this property in any significant degree.

The value of much of the early and some of the later work on this subject is diminished because experimental conditions were not adequately controlled and suitable analytical methods were not then available. An informative documented general review of the hydrolytic scission of



$$-\overset{|}{\underset{|}{\mathrm{P}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{P}}}-$$

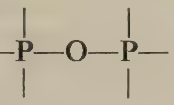
linkages is available[51]; it contains the following list (see Table XII) of environmental factors which influence hydrolysis in aqueous solution, in decreasing order of effectiveness.

*Table XII.—Factors affecting the Rates of Degradation of Polyphosphates*[51]

| Factor | Approximate effect on rate |
|---|---|
| Temperature | $10^5$–$10^6$ faster from freezing to boiling |
| pH | $10^3$–$10^4$ slower from strong acid to base |
| Enzymes | as much as $10^5$–$10^6$ faster |
| Colloidal gels | as much as $10^4$–$10^5$ faster |
| Complexing cations | very many-fold faster in most instances |
| Concentration | roughly proportional |
| Ionic environment in solution | several-fold change |

The hydrolytic scission of the pyrophosphate ion obeys first order kinetics over a wide range of pH, the reaction being acid catalyzed[107–8, 116–20, 182, 185] and having an activation energy of about 23 kcal./mole.

Hydrolysis of the



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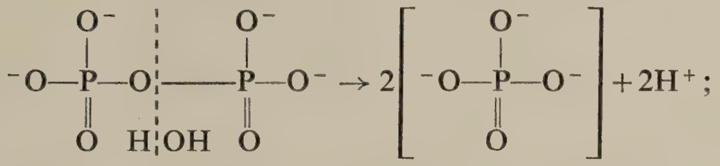
linkage is accompanied by an increase in the acid hydrogen concentration, for example



$$^{-}O-\overset{O^-}{\underset{O}{\overset{|}{\underset{\|}{P}}}}-\underset{H}{O}\,\vdots\,\underset{OH}{\text{———}}\,\overset{O^-}{\underset{O}{\overset{|}{\underset{\|}{P}}}}-O^- \rightarrow 2\left[\,^{-}O-\overset{O^-}{\underset{O}{\overset{|}{\underset{\|}{P}}}}-O^-\right]+2H^+;$$

for rate measurements, it is, therefore, important to control pH, or as some investigators have preferred,[107] to make the determinations by radioactive tracer technique at such low molarities that changes in hydrogen ion concentration can be neglected. Table XIII contains first-order rate constants obtained under controlled pH conditions at the concentrations and by the analytical procedure stated. Further data based on dissociation constants measured under the conditions of the kinetic experiments ($10^{-4}$–$10^{-1}$ M., temperatures, 50–70°C., pH 1·25–6·85, ionic strength 0·301–1·14), are given in reference 184.

When the rate constant at 65·5°C. was plotted against pH a smooth curve was obtained,[117] which is shown in Fig. 6, but later it was reported from a more detailed study of the reversion rates at 60·03°C. over a narrower pH range, that this curve had a stepped portion in the region pH 2 to pH 5, with the rate of hydrolysis rising sharply again over the range pH 1·79 to pH 0·38[108] (see Fig. 7).

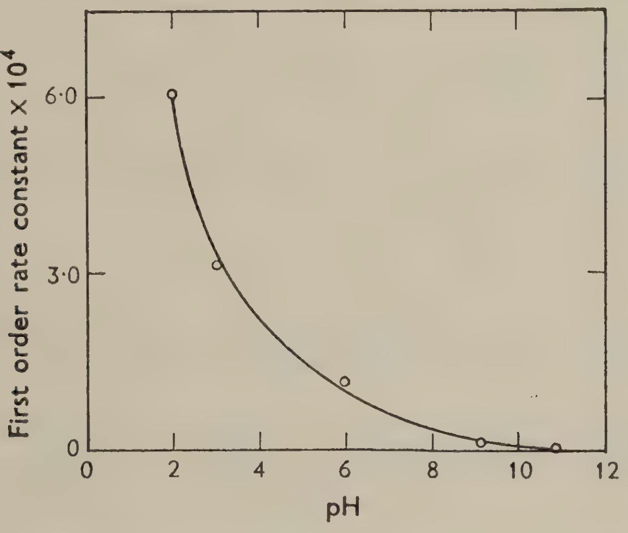


FIG. 6.—Effect of pH on the rate of hydrolysis of sodium pyrophosphate in solution

Attempts have been made to calculate the overall rate constants from a summation of the contributions of individual rate constants of the different ionic species of pyrophosphate present at the particular pH.[98, 107–8, 122] For example, if $k$ represents a rate constant, $x$ the mole fraction of the total pyrophosphate in solution, and the subscripts 4, 3, 2, 1 and 0 refer to the species $H_4P_2O_7$, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$ and $P_2O_7^{4-}$ respectively, then the overall rate constant may be regarded as:

$$k_{\text{obs.}} = k_4x_4+k_3x_3+k_2x_2+k_1x_1+k_0x_0$$

*Table XIII.—First Order Rate Constants, k, min.$^{-1}$, for the Pyrophosphate Ion at Different Temperatures and pH Values*

| 59·87°C.[107] | | 60°C.[116] | | 65·5°C.[117-8] | | 100°C.[119] | |
|---|---|---|---|---|---|---|---|
| pH | $k_{\text{obs.}}$ | pH | $k_{\text{obs.}}$ | pH | $k_{\text{obs.}}$ | pH | $k_{\text{obs.}}$ |
| 0·83 | $2·74 \times 10^{-3}$ | 1·0 | $1·06 \times 10^{-3}$ | 2·0 | $5·36 \times 10^{-4}$ | 1·92 | $4·98 \times 10^{-2}$ |
| 1·01 | $1·80 \times 10^{-3}$ | 4·0 | $1·23 \times 10^{-4}$ | 2·8 | $4·04 \times 10^{-4}$ | 2·07 | $2·07 \times 10^{-3}$ |
| 1·31 | $9·33 \times 10^{-4}$ | | | 3·0 | $3·31 \times 10^{-4}$ | 3·21 | $8·64 \times 10^{-3}$ |
| 1·71 | $4·82 \times 10^{-4}$ | | | 4·9 | $2·99 \times 10^{-4}$ | 7·84 | $4·68 \times 10^{-3}$ |
| 2·01 | $3·37 \times 10^{-4}$ | | | 5·0 | $2·90 \times 10^{-4}$ | | |
| 2·31 | $2·61 \times 10^{-4}$ | | | 6·0 | $1·25 \times 10^{-4}$ | | |
| 2·53 | $2·23 \times 10^{-4}$ | | | 9·3 | $1·0 \times 10^{-5}$ | | |
| 2·71 | $2·00 \times 10^{-4}$ | | | 10·9 | $4·8 \times 10^{-6}$ | | |
| 3·00 | $1·83 \times 10^{-4}$ | | | | | | |
| 3·34 | $1·71 \times 10^{-4}$ | | | | | | |
| $\mu = 0·15$ | | 1% solution | | 0·245 atom weights phosphorus per litre | | — | |
| Isotopic dilution | | Orthophosphate estimated by titration with silver nitrate[121] | | Paper chromatography | | Precipitation of silver salts and titration | |

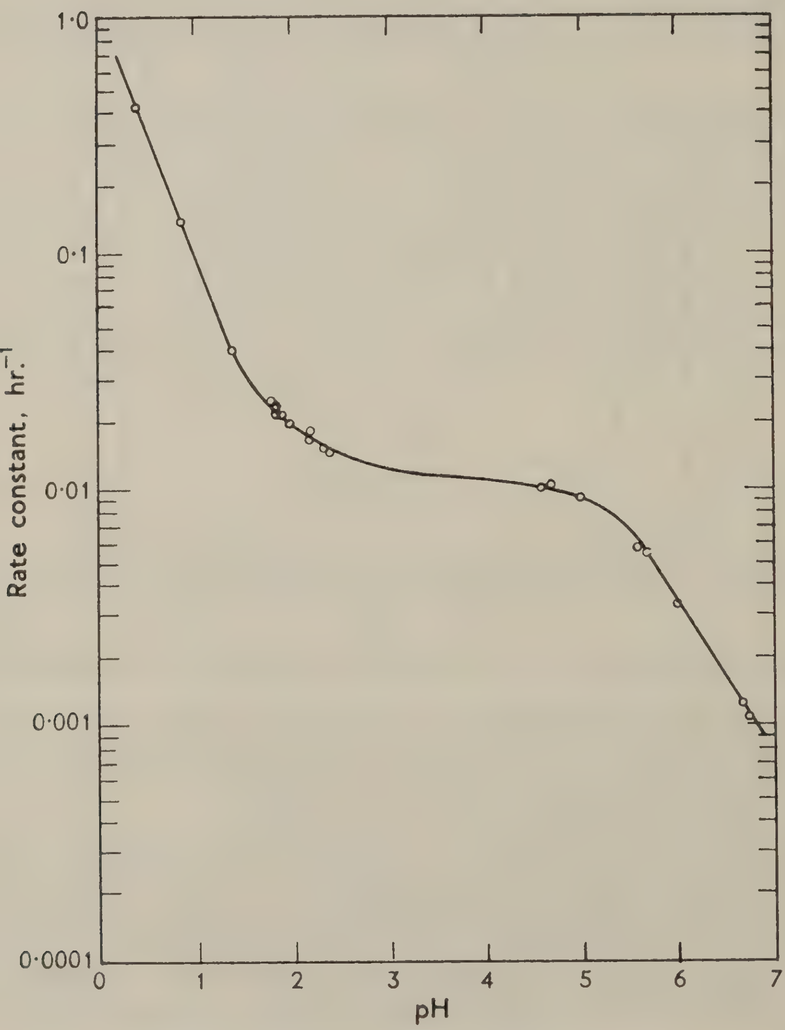


FIG. 7.—Aqueous reversion of pyrophosphate ion at 60·03°C.

However, in order to explain the rapid rise in the rate constant at low pH, it has been suggested that the effect of a second order reaction, involving the hydronium ion, $H_3O^+$, should be considered, although the data were insufficient to test this hypothesis quantitatively.[107] A second explanation has been advanced,[108] based on the data shown in Fig. 7, by which a parameter, $k_5x_5$, additional to those shown in the equation above, is required to give a good fit between observed and calculated rate constants, and which refers to the ionic species $H_5P_2O_7^+$. Such an assumption, if correct, would lead to the proportions of the $H_5P_2O_7^+$ ion, at different pH values, shown in Table XIV.

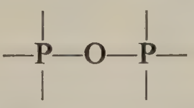
*Table XIV.—% proportion of* $H_5P_2O_7^+$ *Ions at Different pH Values*

| pH | 0·38 | 0·80 | 1·37 | 1·73 | 1·85 |
|---|---|---|---|---|---|
| % $H_5P_2O_7^+$ ion | 92 | 78 | 33 | 11 | 6 |

A similar ionic species, $H_4PO_4^+$, has been suggested to account for abnormalities in the conductivity of pure orthophosphoric acid.[122-3] No evidence could, however, be found for the existence of the metaphosphate ion, $PO_3^-$, as a reaction intermediate. The kinetic form of the hydrolysis and the values of the Arrhenius parameters suggest that the mechanism falls into the A2 category.[185, 186]

The catalytic accelerative effect of metal cations on the hydrolytic degradation of the pyrophosphate ion in neutral solution at 60°C. has been studied[124, 151] and the previous work on this subject reviewed. Kinetic measurements showed that trivalent cations, e.g. $Al^{+++}$, were more effective than divalent, e.g. $Ca^{++}$, $Ba^{++}$ or $Sr^{++}$, or monovalent, e.g. $H^+$, $Li^+$ or $K^+$, and that anions had little effect. However, in the presence of sodium chloride the rate of hydrolysis was slightly reduced at pH 4·5 and markedly slower at pH 2·0. A somewhat higher concentration of magnesium chloride than of sodium chloride was required before noticeable changes in reversion rates occurred. This is not unexpected for the hydrolytic catalyst at low pH is probably $H_3O^+$.[125]

The presence of molybdenum groups within the co-ordination sphere of the phosphorus atoms in pyrophosphoric acid is said to result in instability of the



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linkages,[126] the first order rate constants at 25°C., in N.$H_2SO_4$, for pyro- and molybdopyrophosphoric acids being $4{\cdot}86 \times 10^{-6}$ sec.$^{-1}$ and $1{\cdot}31 \times 10^{-6}$ sec.$^{-1}$ respectively.

Enzymatic phosphatases, under the right conditions, degrade linear polyphosphates quite rapidly and pyrophosphates appear to be hydrolyzed to orthophosphates by passage through the bodies of rats and rabbits.[127]

## TRIPHOSPHORIC ACID, $H_5P_3O_{10}$

Triphosphoric acid occurs in varying amounts as a constituent of polyphosphoric acids containing more than about 72% of phosphoric oxide.[40] Dilute solutions of the pure acid can most readily be prepared by passing a cold solution of the recrystallized sodium salt, $Na_5P_3O_{10}$,$6H_2O$, through a cationic resin ion exchanger.[23, 128]

The successive dissociation constants of acid prepared in this manner have been calculated from its pH-titration curve[101, 106, 129-30]; the first ionization constant is very large, typical values for the others, at infinite dilution at 25°C., being[130]:

$$K_2 = 10^{-1}$$
$$K_3 = 10^{-2{\cdot}3}$$
$$K_4 = 10^{-6{\cdot}50}$$
$$K_5 = 10^{-9{\cdot}24}$$

Calculations of the successive ionization constants of triphosphoric acid have been made, in a manner similar to that described for pyrophosphoric acid,[106] on the basis of structural considerations. Values obtained were in fair agreement with those derived by the author from electrometric titration curves, but did not agree so well with those of other investigators.[101-2, 129-30, 154-6] The possibility of ionization equilibria due to condensation and disproportionation reactions in defined pH ranges, in addition to the normal simple dissociation stages, has been suggested, as with pyrophosphoric acid, to account for the reported discrepancies between the values of p$K$ calculated from titration curves.[106]

Values of the free energy, enthalpy and entropy of ionization of triphosphoric acid have been reported.[157, 181]

The hydrolytic degradation of the triphosphate ion has been studied under a wide variety of conditions and is affected by the same factors as those already described under pyrophosphoric acid. Although quite stable at room temperature in aqueous solution at pH 7 to pH 9, $P_3O_{10}^{5-}$ undergoes rapid hydrolytic breakdown under more acid conditions and at high temperatures, in two stages:

$$(a) \qquad [P_3O_{10}]^{5-} + H_2O \rightarrow [HP_2O_7]^{3-} + [HPO_4]^{2-}$$

$$(b) \qquad [HP_2O_7]^{3-} + H_2O \rightarrow [HPO_4]^{2-} + [H_2PO_4]^{1-}$$

Both stages of the hydrolysis are first order reactions over the range pH 2·0 to pH 12·0, the latter proceeding independently of the former at about one-third the rate[117] (see also Refs 121, 149, 187).

*Table XV.—Overall First Order Rate Constants, k, min.$^{-1}$, for the Triphosphate Ion at Different pH Values at* 65·5°C.[117]

| pH | $k$, min.$^{-1}$ |
|---|---|
| 2·0 | $2{\cdot}19 \times 10^{-3}$ |
| 3·0 | $9{\cdot}4 \times 10^{-4}$ |
| 5·0 | $2{\cdot}89 \times 10^{-4}$ |
| 9·3 | $1{\cdot}5 \times 10^{-5}$ |
| 12·0 | $1{\cdot}41 \times 10^{-4}$ |

Reversion rates for the triphosphate ion at 65·5°C., at a concentration equivalent to 0·0951 moles of phosphorus per litre, are contained in Table XV and shown graphically in Fig. 8.

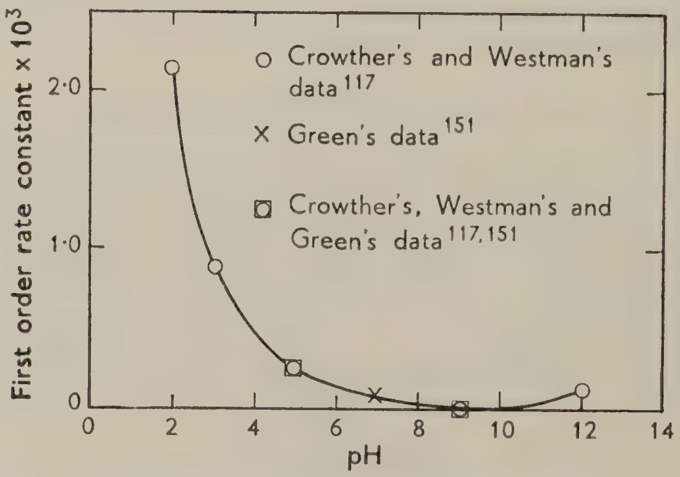


FIG. 8.—Effect of pH on the rate of hydrolysis of sodium triphosphate in solution

## TETRAPHOSPHORIC ACID, $H_6P_4O_{13}$, AND OTHER LINEAR POLYPHOSPHORIC ACIDS OF THE GENERAL FORMULA $H_{n+2}P_nO_{3n+1}$

Tetraphosphoric acid occurs, along with other polyphosphoric acids, when the concentration of phosphoric oxide in the mixture exceeds about 76%[40]; the pure acid could, in principle, be obtained by ion exchange from the neutral hexaguanidinium, the dihydrogen-tetra-acridinium[131] or the ammonium salt,[132-3] which can be prepared substantially free from other phosphate species by alkaline cleavage of cyclic sodium tetrametaphosphate in aqueous solution at not too high temperatures.

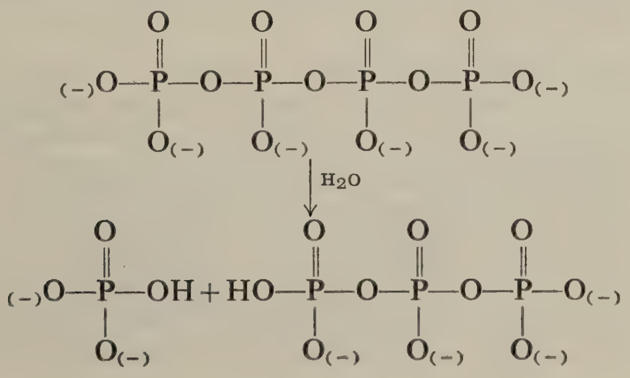
Dilute solutions of more highly polymerized acids have been obtained by the ion-exchange technique from long-chain phosphates including those known as Kurroll, Maddrell or Graham salts.[134-8]

As outlined in Table I, tetraphosphoric acid has a linear chain structure and its electrometric titration curve shows it to possess four strongly and two weakly dissociated hydrogen ions; some tentative values have been calculated for the ionization constants for some of the stages of both tetra- and so-called hexaphosphoric acids from electrometric titration data,[106] but these are not confirmed by independent measurements.[102,158] A selection of these is given in Table XVI, and values for pyrophosphoric acid and triphosphoric acid are included for comparison. As expected, values of $pK_N$ decrease and values of $pK_{N-1}$ increase with increasing chain length in the series of polyphosphoric acids $H_NP_{N-2}O_{3N-5}$. An exception to this rule is the anomalously low value for $pK_{N-1}$ in $H_5P_3O_{10}$; it is possible that the configuration of the $HP_3O_{10}^{4-}$ ion is particularly stable[158] since similar anomalies have been observed in its N.M.R. spectrum.[159] There is some evidence that free polyphosphoric acids are only dissociated to about 30% in aqueous solution, although all the hydroxyl groups present except the two terminal ones behave as strong acids on titration.[188]

*Table XVI.—Ionization Constants for Chain Polyphosphoric Acids* $H_NP_{N-2}O_{3N-5}$ *at 25°C. and Ionic Strength* $\mu = 1$

| Acid | N | $pK_N$ | $pK_{N-1}$ | $pK_{N-2}$ | $pK_{N-3}$ | Reference |
|---|---|---|---|---|---|---|
| Pyrophosphoric | 4 | 8·7 | 6·0 | 2·0 | 1·7 | 102 |
| Triphosphoric | 5 | 8·6 | 5·7 | 2·0 | 1·2 | 102 |
| | | 8·8 | 5·8 | 2·1 | 1·1 | 158 |
| Tetraphosphoric | 6 | 8·3 | 6·6 | 2·2 | 1·4 | 158 |
| 'Hexaphosphoric' | 8 | 8·1 | 6·0 | 2·2 | 2·1 | 102 |
| | 18 | 8·1 | 6·5 | 2·9 | 2 | 102 |
| | 62 | 8·2 | 7·2 | — | — | 102 |

The hydrolytic degradation of the tetraphosphate anion, $P_4O_{13}^{6-}$, has been studied; it follows first-order kinetics for most of the course of the reaction,[133] the cleavage occurring predominantly at the ends of the chain to form ortho(mono)- and triphosphate ions, respectively, e.g.,



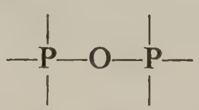
Some evidence has been reported for an alternative route for hydrolytic degradation,[131,139] namely attack on the middle oxygen bridge to form two pyrophosphate ions. However, on account of the limitations of the analytical methods employed and because of the obscuring effect of the rapid hydrolysis of the triphosphate ion produced by the first route, especially at low pH, it is thought likely that hydrolysis of the tetraphosphate ion occurs almost exclusively by the attack of water on an end oxygen bridge,[133] and that pyrophosphate arises from a bimolecular reaction between the orthophosphate and triphosphate so formed.[191] However, there is good evidence that pentaphosphate and hexaphosphate degrade by two routes, the first and faster producing orthophosphate, together with a polyphosphate chain shorter by one $PO_4$ unit, while the second produces trimetaphosphate with a chain shorter by three units.[189,191] The first mechanism is catalyzed by the copper(II) chelate of poly-*L*-lysine, and the second by the copper(II) chelate of ethylenediamine.[190] The yield of trimetaphosphate increases with polyphosphate chain length[191] (see Section XXVII, page 756).

The tetraphosphate ion is less stable than the triphosphate ion over the whole pH range; typical values for the overall constant, at 65·5°C. and a concentration of 0·17 atom weights of phosphorus per litre, are contained in Table XVII.[133]

*Table XVII.—Overall First Order Rate Constants, k, min.⁻¹, for the Tetraphosphate Ion at Different pH Values, at* 65·5°C.[133]

| pH | $k$, min.$^{-1}$ |
|---|---|
| 2·55 | $1{\cdot}8\times10^{-3}$ |
| 5·35 | $8{\cdot}3\times10^{-4}$ |
| 9·8 | $2{\cdot}5\times10^{-4}$ |
| 13·3 | $2{\cdot}5\times10^{-4}$ |

The interpretation of the mechanism of the hydrolytic degradation of polyphosphoric acids and their salts, with chains longer than tetraphosphoric acid, has proved difficult because of the variety of routes available for the process to occur. During the hydrolysis of polyphosphates of medium chain length, $n \geqq 5$, in not too acid media, pH $\geqslant 3{\cdot}5$, the formation of cyclic anions has been observed[140-2] and possible mechanisms for this phenomenon have been discussed.[142-5] In acid solutions, the hydrolysis of long chain polyphosphates is thought to proceed, to an increasing extent, by cleavage of middle



$$-\overset{|}{\underset{|}{P}}-O-\overset{|}{\underset{|}{P}}-$$

linkages, compared with the lower members of the series, thus leading to the formation of mixtures of polyphosphates with smaller degrees of condensation.[144-5] The mechanism is said to involve splitting off $PO_3^-$ groups as the activated complex.[30] Typical overall first-order rate constants and half-life times, at 60°C., for a long-chain polyphosphate ion with an average chain length of 1000, are given in Table XVIII.[30,147]

*Table XVIII.—Overall First Order Rate Constants, k, min.⁻¹, for Long Chain Polyphosphate Ion, at* 60°C., *at Different pH Values and Half-life Times*

| pH | $k$, min.$^{-1}$ | Half-life times |
|---|---|---|
| 1 | $30{\cdot}4\times10^{-3}$ | 22·8 min. |
| 3 | $1{\cdot}72\times10^{-3}$ | 6·7 hr. |
| 5 | $\sim0{\cdot}10\times10^{-3}$ | 4·4 days |
| 8 | $0{\cdot}011\times10^{-3}$ | 45·4 days |

A procedure has been described, involving solvent extraction and ion exchange by which gram quantities of essentially pure tetra-, penta-, hexa-, hepta-, and octaphosphoric acid have been prepared from a mixed polyphosphoric acid. The corresponding phosphates were hydrolyzed at pH values of 4, 7, and 11, and temperatures of 30° and 60°C. First-order specific rate constants were determined for the overall degradation of each species (see Fig. 9 for data at 60°), and for the separate degradation routes involving the splitting off of one- and three-phosphorus fragments. The activation energies for these processes were also given and discussed. It was shown that the specific rate constants for orthophosphate (end group) removal are a regular function of the number of electrons in outer valence shells divided by the number of P–O–P linkages: e.g. from $P_2O_7^{4-}$ (56 electrons, 1 P–O–P) to $P_8O_{25}^{10-}$ (200 electrons, 7 P–O–P's).[192]

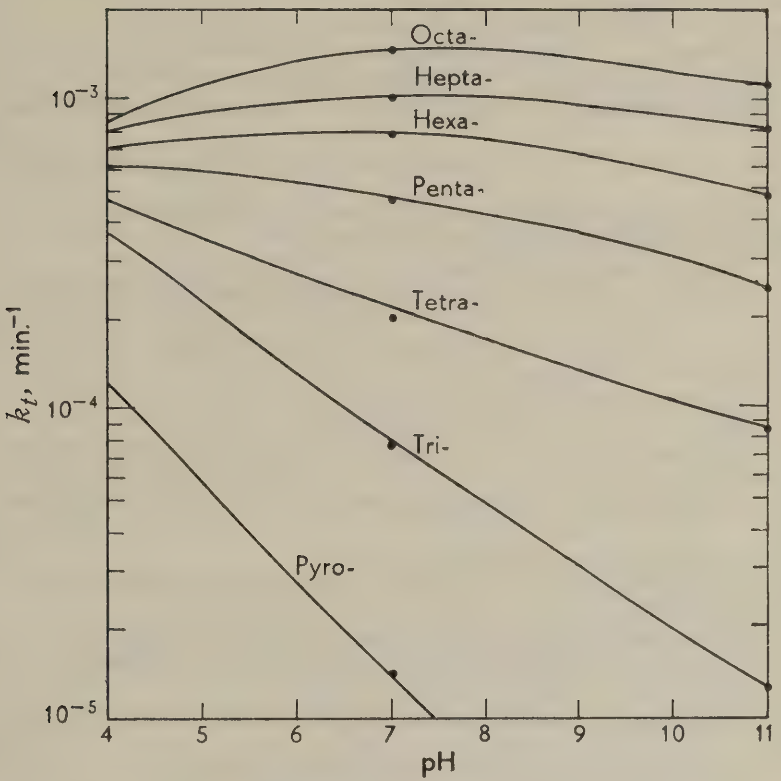


FIG. 9.—Specific rate constants for sodium polyphosphates as a function of pH at 60°: pyro- and tri- values from ref. 116

The 'glacial metaphosphoric' acids of commerce, often used as reagents for the precipitation of proteins,[147–8] contain up to 18% of sodium oxide, $Na_2O$, in addition to phosphoric oxide and water, in order to render the otherwise very sticky viscous acids easier to handle.[37, 149–50] Pure acids with a composition corresponding closely to $HPO_3$ contain branching points, are not regarded as truly linear polyphosphoric acids, and are discussed more fully in Section XXVII (page 755).

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## SECTION XXVII

# CYCLIC AND BRANCHED POLYPHOSPHORIC ACIDS

BY J. E. SUCH

THE combination of middle group phosphate structural units (see page 727), can be regarded as the basis of the formation of:

(*a*) ring molecule ions, the cyclic polyphosphates, to which branching points may be introduced to attach;
(*b*) rings to chains, and finally to form;
(*c*) cross-linked polymers, by introducing branching points into linear polyphosphates.

(*a*) The well-known cyclic trimetaphosphate and tetrametaphosphate anions, for example, shown in Fig. 1, are metaphosphates, for their composition is $(PO_3)_n^{n-}$ and they are not to be confused with the polymeric polyphosphate anions $(P_nO_{3n+1})^{(n+2)-}$, of which the ends of the chains are terminated by hydroxyl groups (Section XXVI).

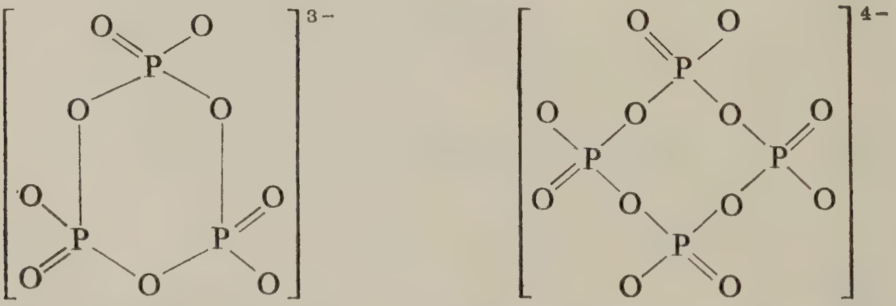


FIG. 1.—The cyclic trimetaphosphate, $(PO_3)_3{}^{3-}$, and tetrametaphosphate, $(PO_3)_4{}^{4-}$, anions

(*b*) Molecule ions, with one or more branching points linking chains to rings, of the type shown in Fig. 2, which are isomeric with their wholly cyclic counterparts,

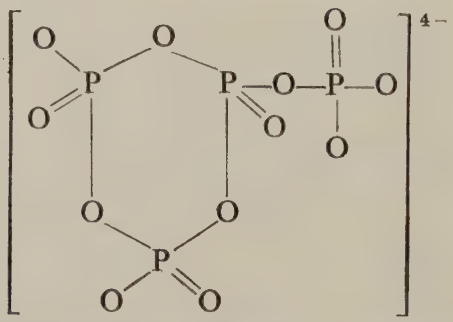
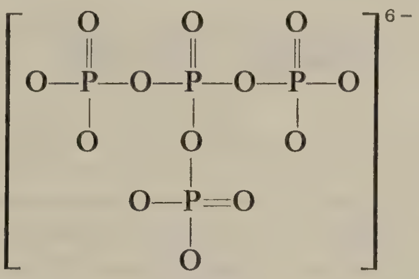


FIG. 2.—Polyphosphate ion containing ring and chain (*iso*-tetrametaphosphate ion $(P_4O_{12})^{4-}$)

Refs. p. 758

have been suggested, the example quoted, in particular, being considered a transitory intermediate in the stepwise hydration of phosphoric oxide (see Section X, page 394). Neither the acid formulated in Fig. 2 nor its salts has been individually characterized. It was formerly proposed that etherolysis of phosphoric oxide produced compounds of this type, in which OH was replaced by OR,[1-2] but more recent work has disclosed only straight chain polyphosphoric acids and esters.[45]

(*c*) Branched, or cross-linked polyphosphoric acids, sometimes referred to as ultraphosphoric acids, are usually defined as acids in which the ratio of $H_2O/P_2O_5$ is less than unity, and are thought to contain branching points at which tertiary $PO_4$ tetrahedra are linked by three of their oxygen atoms to neighbouring phosphorus atoms.[3-5] A simple example of an acid of this type is the hypothetical *iso*-tetraphosphoric acid, postulated in the stepwise hydrolytic degradation of phosphoric oxide, and shown in Fig. 3.



$(P_4O_{13})^{6-}$

FIG. 3.—The *iso*-tetraphosphoric acid ion

It has also been suggested[6] that cross-linkage of chain polymers can occur by loss of water, on condensation, as in Fig. 4.

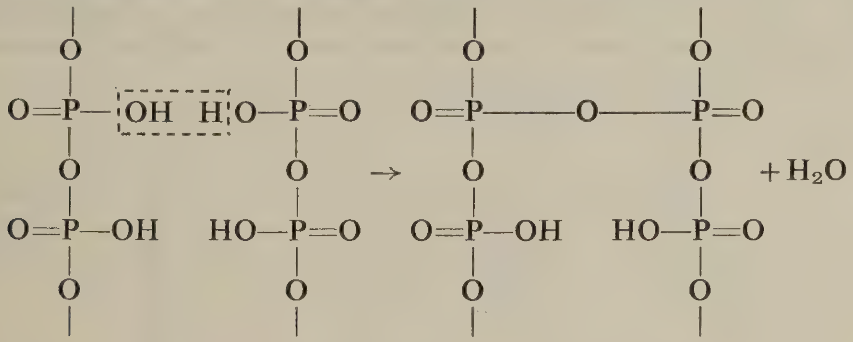


FIG. 4.—Cross-linkage of linear polyphosphates

The consequences of the hydrolysis of compounds having these two types of cross-links have been discussed in terms of the acid strength of the resultant (OH) groups.[5]

In contrast to the –P–O–P– linkages in linear and cyclic polyphosphate anions, those of the bridges in the cross-linked species are much more readily hydrolyzed in aqueous solution. Such behaviour was predicted from theoretical considerations[3] and verified by measurements of the rate constant for the hydrolytic cleavage of –P–O–P– linkages which converted a branching point into a middle group.[7-8] The rate of hydrolysis is about a thousand times faster for branching points than for linkages in the middle or at the end of chains, and is practically independent of the concentration, pH, ionic strength and presence of added salts.

The existence of branching points in compounds suspected of containing them can be deduced from the rapid drop in viscosity and parallel increase in the pH value of their aqueous solutions, both being caused by this ready hydrolysis.[9-10]

The cyclic tri- and tetra-metaphosphoric acids may be prepared[3,11-5]:

(*a*) from dilute aqueous solutions of the corresponding sodium salts by passage through hydrogen ion-exchangers (though it would be difficult to concentrate them further owing to their hydrolytic instability).

(*b*) by decomposition of their relatively insoluble corresponding heavy metal salts, for example of lead or copper, by passing hydrogen sulphide into a suspension in water, filtering off the heavy metal sulphide and removing the excess of hydrogen sulphide in vacuo at low temperature.

Both trimeta- and tetrameta-phosphates have been identified by chromatographic analysis as minor constituents of solutions prepared from polyphosphoric acid containing more than 86·1% of phosphoric oxide,[5] or from sodium polyphosphates of Na/P ratio 0·71–0·88.[46] It is possible, however, that they may have arisen from extensively cross-linked acids, similar to those described earlier, by hydrolysis during the preparation of the samples for analysis.[16] Alternatively they may arise from the hydrolysis of linear polyphosphates, which at pH 6 has been shown to yield cyclic anions, principally trimetaphosphate, as shown in the table below.[52]

*Yield of trimetaphosphate from the degradation of polyphosphates of varying chain length* (*pH*$=6$; t$=80$°C.)

| Chain length *n* | 2–4 | 5 | 6 | 7 | 8 | ∞ |
|---|---|---|---|---|---|---|
| Yield of trimetaphosphate in % P | 0 | 5–8 | 15–17 | ~25 | ~38 | ≥60 |

Partial hydrolysis of the volatile (H) form of phosphoric oxide, $P_4O_{10}$, by long-chain polyphosphoric acids, instead of by water, could also lead to the formation of ring compounds more complex than those typified in Fig. 2.[16] However, tetrametaphosphoric acid is the main product of the hydrolysis of phosphoric oxide by an excess of water in an organic medium, whilst limited amounts of water yield linear polyphosphoric acids of varying molecular weights.[44]

Since all the hydroxyl groups of the cyclic polyphosphoric acids have practically the same large dissociation constants, they may be considered as strong acids; in consequence, their electrometric pH titration curves show a single strong inflection,[17–20] similar to that given by hydrochloric acid, for example (Fig. 5).

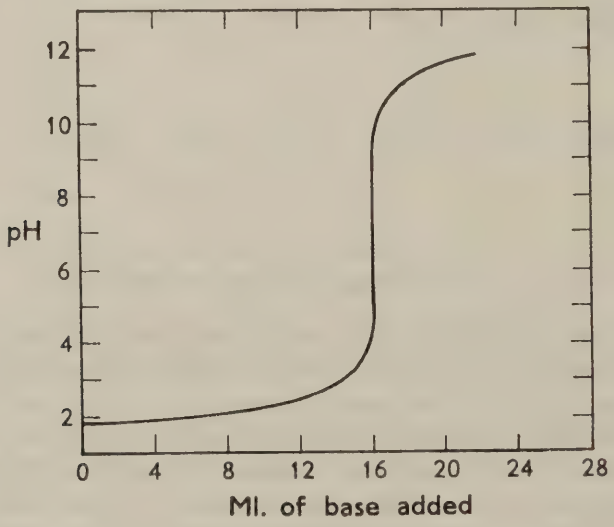


FIG. 5.—pH titration of trimetaphosphoric acid

From potentiometric titration curves, the values calculated at 25°C. for all three thermodynamic ionization constants, $pK_1$, $pK_2$ and $pK_3$, of trimetaphosphoric acid are very large,[21] but the fourth hydrogren ion of tetrametaphosphoric acid is reported to be appreciably weaker than the other three[22] and a value of 2·78 for $pK_4$ has been quoted.[21]

Measurement of the conductance of dilute solutions of trimeta- and tetrametaphosphoric acids indicates that they dissociate into singly charged ions and triply or quadruply charged ions respectively and thus supports the tri- and tetra-meric formulation of these compounds.[22] The rate of inversion of sucrose in $H_3P_3O_9/Na_3P_3O_9$

or $H_4P_4O_{12}/Na_4P_4O_{12}$ solutions at 25°C. could also roughly be interpreted on the same basis, although the values of $K_1$ obtained were about twice those deduced from the conductimetric experiments. The new value of $K_1$ (trimetaphosphate) also accounted well for the effect of trimetaphosphate on the kinetics of the chromate–iodide and iodate–iodide reactions.[47]

Whilst practically stable at 20°C. under neutral conditions, cyclic trimetaphosphate and tetrametaphosphate ions readily hydrolyze in acidic aqueous solution. The hydrolytic degradation follows a first-order law as long as the pH is held constant, and proceeds in stages, the reaction rate for each of which is strongly temperature and pH dependent, the magnitude of the effect varying for the successive reactions:

$$(a) \quad (P_3O_9)^{3-} + H_2O \rightarrow (H_2P_3O_{10})^{3-} + H_2O \rightarrow (H_2P_2O_7)^{2-} + (H_2PO_4)^{-} + H_2O \rightarrow 3(H_2PO_4)^{-} \quad ^{23-9}$$

$$(b) \quad (P_4O_{12})^{4-} + H_2O \rightarrow (H_2P_4O_{13})^{4-} + H_2O \rightarrow (H_2P_3O_{10})^{3-} + (H_2PO_4)^{-} + H_2O \rightarrow (H_2P_2O_7)^{2-} + 2(H_2PO_4)^{-} + H_2O \rightarrow 4(H_2PO_4)^{-} \quad ^{24-5,28,30-4}$$

The ammonolysis of tetrametaphosphate yields, *inter alia*, ammonium triphosphate.[48]

Many values for first-order reaction constants for the hydrolytic degradation of cyclic polyphosphate anions are available in the references given; they are not quoted here, as varying conditions under which the measurements were made render comparisons difficult. However, the following tabulation by Thilo[35] and others,[49] Table I, contains useful typical comparative data for first order reaction constants, half-life values and activation energies, for the different types of polyphosphate ions described in this and other Sections.

*Table I.—Kinetic Constants for the Hydrolytic Degradation of Various Polyphosphate Anions*

| Type of anion | pH | °C. | First order $k \times 10^3$ min.$^{-1}$ | Half-life value | Activation energy kcal./mole |
|---|---|---|---|---|---|
| Cyclic trimetaphosphate $(P_3O_9)^{3-}$ | 1 | 60 | 39·8 | 17 min. | |
| | 3 | 40 | 0·03 | | |
| | | 60 | 0·29 | 1·7 days | 21·8 |
| | 5 | 60 | 0·04 | 15·1 days | |
| | 7 | 60 | 0·0069 | 69·3 days | |
| | | 80 | 0·026 | | 19·6 |
| Cyclic tetrametaphosphate $(P_4O_{12})^{4-}$ | 1 | 40 | 0·67 | | |
| | | 60 | 4·71 | 2·48 hr. | 20·0 |
| | 3 | 50 | 0·027 | | |
| | | 60 | 0·072 | 6·5 days | 20·0 |
| | 7 | 60 | 0·003 | 116·5 days | |
| Cyclic hexametaphosphate $(P_6O_{18})^{6-}$ | 4 | 30 | 0·00035 | > 1 yr. | 9 |
| | | 60 | 0·0013 | ,, | |
| | 7 | 30 | 0·00036 | ,, | 6 |
| | | 60 | 0·0009 | ,, | |
| | 11 | 30 | 0·00032 | ,, | 6 |
| | | 60 | 0·00096 | ,, | |
| Linear polyphosphate $(P_nO_{3n+1})^{(n+2)-}$ $n \geqq 3$ | 1 | 40 | 7·04 | | |
| | | 60 | 30·4 | 22·8 min. | 15·1 |
| | 3 | 40 | 0·19 | | |
| | | 60 | 1·72 | 6·7 hr. | 22·8 |
| | 5 | 60 | ~0·10 | 4·4 days | |
| | 8 | 60 | 0·0106 | 45·4 days | 25·0 |
| Branched polyphosphates | Independent of pH | 40 | 26 | | 15·4 |

**Refs. p. 758**

Under comparable conditions the cyclic hexametaphosphate ion is more stable than any of the others which have been investigated. The low value of the activation energy observed in this case, corresponding to a decreased influence of temperature on the hydrolysis, may be due to the ability of the large and flexible hexametaphosphate ring to absorb thermal energy without rupture.[49] As with linear polyphosphate ions, the hydrolytic stability of the cyclic anions is greatly reduced in the presence of added cations[26, 36-8] and enzymes.[41] Cyclic phosphoric acids are also rapidly decomposed by an excess of hydrogen peroxide[50] or by fluoride ions.[51] In the latter case the $(FP_3O_9)^{4-}$ and the $(FP_4O_{12})^{5-}$ ions are formed from trimetaphosphate and tetrametaphosphate respectively.

The hydrolytic scission of –P–O–P– linkages of all types has been extensively reviewed.[39]

The alkali metal salts of trimetaphosphoric and tetrametaphosphoric acids are readily soluble in water, but those of the alkaline earth metals are not; collected references to these salts are available.[39]

Although the presence of cyclic anions containing as many as six to eight phosphorus atoms has been inferred from the paper chromatographic analysis of aqueous hydrolysates of phosphate glasses,[40-2] so far only the cyclic hexametaphosphate has been isolated from the $LiPO_3$–$Li_4P_2O_7$ system. The free acid was liberated by ion exchange, and isolated as the sodium salt $(NaPO_3)_6,6H_2O$.[49]

Cross-linked polyphosphoric acids containing branching points may be prepared by thermal dehydration of acids with higher water contents. For example, when orthophosphoric acid is heated in a platinum–gold alloy container to about 450°C. at atmospheric pressure, the product on cooling forms a glassy solid containing cross-linked in addition to linear polyphosphoric acids.[6, 43]

Azeotropic phosphoric acid, b.p. 864°C. at 760 mm., has a mole ratio $H_2O/P_2O_5$ of 0·65 and is believed to be highly cross-linked, for when the solidified transparent glass is put into water it decrepitates and breaks up into fibrous fragments. This behaviour is thought to be connected with the rapid hydrolysis of branching points near the surface of the solid glass, and consequent strain in the structure.[6, 39] It has been calculated that as much as one-third of all the phosphorus atoms in such a glassy polyphosphoric acid are linked by branching points to their neighbours.[39]

Polyphosphoric acids with more than the azeotropic composition of 92% $P_2O_5$ can be prepared by combining a small amount of water or orthophosphoric acid with phosphoric oxide, but little is known about these compounds which probably approach in character the vitreous forms of phosphoric oxide itself.

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## SECTION XXVIII

# AMIDO- AND IMIDO-PHOSPHORIC ACIDS AND THEIR SALTS

BY D. A. PALGRAVE

### Nomenclature

CONSIDERABLE divergences of opinion exist regarding the nomenclature of the oxyacids of phosphorus in which partial replacement of the oxygen atoms by amido or imido groups has taken place. A serious attempt at unambiguous nomenclature was made by Audrieth *et al.*[1] on the basis of a more general system for nitrogen compounds.[2] Typical examples of this system include:

| $PO(NH_2)(OH)_2$ | $PO(NH_2)_2OH$ |
|---|---|
| amidophosphoric acid | diamidophosphoric acid |

$PO(NH_2)_3$
phosphoryl triamide

| $(HO)_2PO(NH)PO(OH)_2$ | $(HO)_2PO(NH)PO(OH)NHPO(OH)_2$ |
|---|---|
| imidodiphosphoric acid | di-imidotriphosphoric acid |

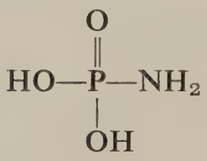
$(HO)_2PO(NH)PO(OH)(NH)PO(OH)(NH)PO)OH)_2$
tri-imidotetraphosphoric acid

However, subsequent usage indicates that this system of nomenclature has not found universal adoption. Recent convention favours the terms 'phosphoramidic' and 'phosphorodiamidic' instead of 'amidophosphoric' and 'diamidophosphoric', particularly when referring to organic derivatives of these acids. The cyclic compounds are normally called 'metaphosphimic acids' rather than 'phosphonitrilic acids', the simple prefixes tri- or tetra- being used to denote the degree of polymerization. Infrared evidence[21] indicates the presence of

$$-\underset{\displaystyle H}{\underset{|}{N}}-$$

groupings in these ring compounds and has rendered the term phosphonitrilic acid inappropriate.

## MONOAMIDOPHOSPHORIC (PHOSPHORAMIDIC) ACID AND ITS SALTS



$$HO-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OH}{\underset{|}{P}}}}-NH_2$$

### Formation and Preparation

The techniques discovered by Stokes (*Mellor*, VIII, 705) remain the most satisfactory methods of preparing the monoamidophosphates. The use of primary and secondary amines instead of ammonia has been shown to produce compounds containing substituted amido groups.

A monofluorophosphate may be used in place of a monochlorophosphate derivative to prepare monoamidophosphate.[3] The reaction takes place at 90°–110°C. at a pressure of 5–20 atm., in the presence of sodium hydroxide:

$$Na_2PO_3F + \tfrac{1}{2}H_2O + NH_3 \rightarrow Na_2PO_3NH_2,\tfrac{1}{2}H_2O + HF$$

Disodium monoamidophosphate is also formed by the interaction of a 60:40 sodamide:potassamide mixture with sodium trimetaphosphate. Recrystallization of the crude reaction product from aqueous acetic acid gives pure sodium hydrogen amidophosphate which can be reconverted to crystalline disodium amidophosphate hexahydrate by neutralization with sodium hydroxide and precipitation with alcohol. The anhydrous salt results from the dehydration of the hydrate at 60–110°C. and 15 mm.[125]

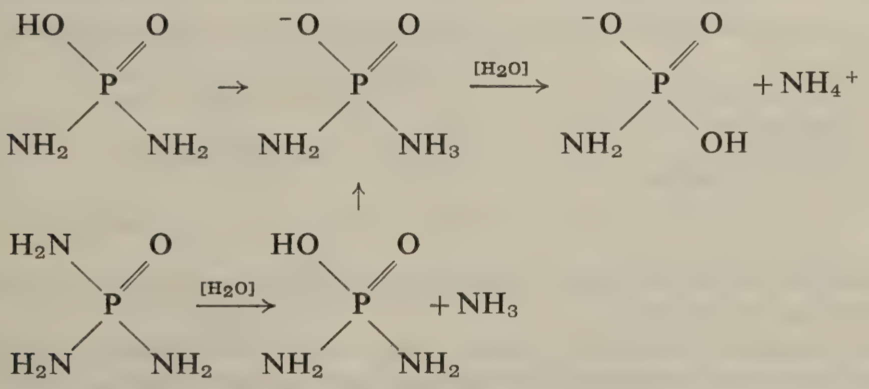
Monoamidophosphoric acid has been obtained in 51% yield by the catalytic hydrogenation of diphenyl phosphoramidate in the presence of platinum dioxide.[4] This is an improvement on the original method of Stokes, and enables several of his stages to be by-passed. The acid may be prepared from its salts either by ion exchange[5] or by displacement using a stronger acid such as perchloric acid.[6] The monohydrate, $H_2PO_3NH_2,H_2O$, decomposes to the anhydrous acid and water at 31°C.[29]

Many investigators have studied the reaction between phosphorus pentoxide and ammonia. There is considerable variation in the reported results. Under exceedingly dry conditions no reaction between gaseous ammonia and solid phosphorus pentoxide could be detected,[7] although this is contrary to the reports of other observers. It had been maintained[8] that a thin film formed on the surface of the phosphorus pentoxide retarded further absorption, but this was not confirmed.[9] In general glassy substances are obtained as reaction products which contain a variety of species including monoamidophosphates.[10] Claims have been made that pure monoamidophosphoric acid can be manufactured in this way.[11] However, most authorities in this field have concluded that this reaction usually results in the formation of polyamidoimidopolyphosphates (*q.v.*) or polymetaphosphimates (*q.v.*), together with some ammonium polyphosphates. The reaction of alkali metal amides with phosphorus pentoxide in an inert medium at ~200°C. gives good yields of phosphoramidates.[126]

Monoamidophosphates are readily obtained from other monoamidophosphates by metathesis[12]:

$$Ag_2PO_3NH_2 + 2NaBr \rightarrow 2AgBr + Na_2PO_3NH_2$$

Unique methods of preparing ammonium salts exist, as the amido group is fairly readily converted to ammonia or the ammonium ion. Thus the action of moist air on diamidophosphoric acid[13] or phosphoryl triamide[14] yields monoammonium monoamidophosphate:



Such zwitter-ion formation appears to be a feature of this class of compounds.

## Physical Properties

The infra-red spectra of several monoamidophosphates have been examined.[15, 21, 30, 82] The principal absorption regions are listed in Table I.

*Table I.—Infra-red Absorption Spectra of Monoamidophosphates*

| Absorption region (cm.$^{-1}$) | Assignment |
|---|---|
| 3500–3200 | $\nu_{as}NH_2$ |
| 3070–2860 | $\nu_{as}NH$ |
| 2610–2450 | $\nu_{s}NH_3$ |
| 1700–1600 | $\omega\delta_{as}NH_3$ |
| 1480–1435 | $\delta_{s}NH_3$ |
| 1205–1160 | $\rho NH_3$ |
| 1195–1130 | $\nu_{as}PO_3$ |
| 1075–1070 | $\rho NH_2$ |
| 1020 | $\rho NH_3$ |
| 1023–993 | $\nu_{s}PO_3$ |
| 845–710 | $\nu PN$ |
| 550–527 | $\delta_{s}PO$ |
| 515–500 | $\delta_{as}PO$ |

The silver and zinc salts are somewhat anomalous, exhibiting low frequencies associated with stretching and internal deformation of the N–H groups and no absorption corresponding to external N–H deformation. This suggests the possibility of some metal–nitrogen coordination within these compounds. In the disodium salt $Na_2PO_3NH_2$[82] the $NH_2$ bending and rocking vibrations are assigned at 1610 and 1098 cm.$^{-1}$ respectively. The symmetrical and antisymmetrical $PO_3$ stretching vibrations are assigned at 980 and 1141/1188 cm.$^{-1}$ respectively. The assignment of symmetrical and asymmetrical stretching frequencies to $NH_3$ groups is substantiated by an *X*-ray diffraction study of monosodium monoamidophosphate.[16]

Its structure, determined by three-dimensional Fourier synthesis, indicates that each phosphorus atom is surrounded by one nitrogen and three oxygen atoms disposed tetrahedrally. There is threefold symmetry about the P–N bond compatible with a trihedral distribution of hydrogen atoms about the nitrogen atom. Hydrogen bonding is thought to take place between any one nitrogen and the oxygen atoms in three adjacent anions. Thus zwitter-ions exist in the solid state in this three-dimensional framework (see Figs. 1 and 2). The crystallographic data are summarized in Table II.

*Table II.—Crystallographic Data for Monosodium Monoamidophosphate*

| | |
|---|---|
| System | Hexagonal, 2 molecules per cell |
| Unit cell dimensions | $a$ 5·773 ± 0·003 $b$ 6·031 ± 0·003 A. |
| Space group | $P6_3$ |
| Indicatrix | Uniaxial—optically negative |
| Refractive indices | $\omega$ 1·56 $\epsilon$ 1·52 |

The structure of this ion bears a striking resemblance to that of the isoelectronic sulphamate ion, $NH_3{}^+SO_3{}^-$.

Nuclear magnetic resonance spectra for mono- and disodium monoamidophosphates have been observed;[22-3] relevant data are tabulated on p. 182 together with corresponding data for related compounds.

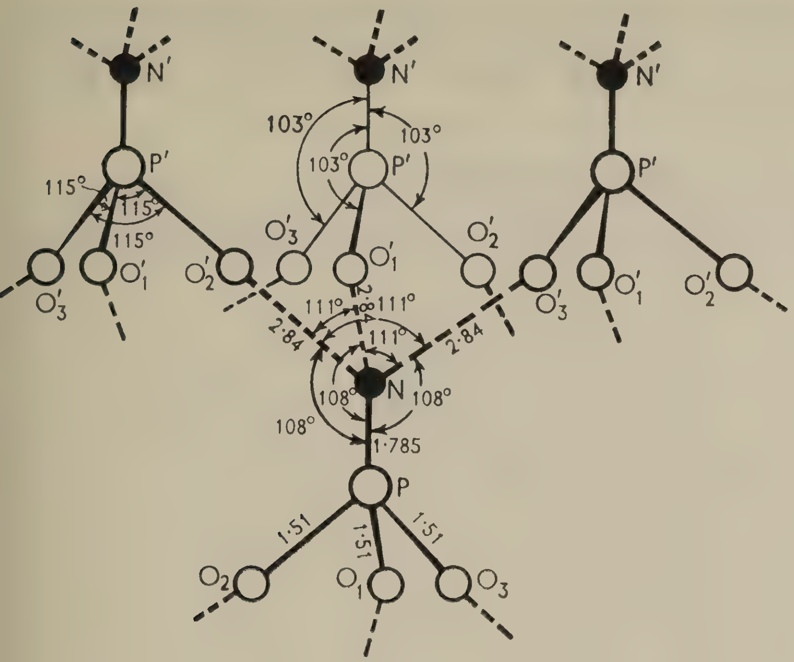


Fig. 1

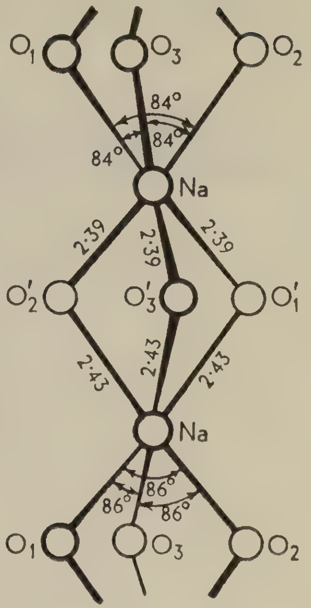
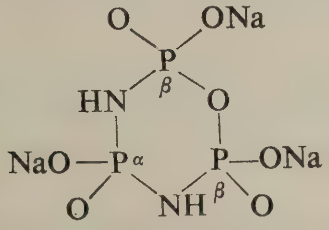


Fig. 2

FIG. 1.—Environment of the phosphoramidate ion. N–H–O bonds shown broken. All distances in A. and all angles in degrees

FIG. 2.—Coordination of $Na^+$ ions. All distances in A. and all angles in degrees

*Table III.—N.M.R. Data for Amidophosphates and Related Compounds*

| Compound | Chemical Shift (p.p.m.)* | Reference |
|---|---|---|
| $(NaO)_3PO$ | −6·0 | 127 |
| $(NaO)_2P(O)NH_2$ | −8·9 | 22, 23, 127 |
| $(NaO)HOP(O)NH_2$ | −3·0 | 22, 23, |
| $NaOP(O)(NH_2)_2$ | −14·5 | 127, 128 |
| $HOP(O)(NH_2)_2$ | +0·2 | 128 |
| | +3·5 | 23 |
| $PO(NH_2)_3$ | −22·0 | 127 |
| $(NaO)_3PS$ | −33·8 | 127 |
| $NaOPS(NH_2)_2$ | −54·2 | 127, 128 |
| $PS(NH_2)_3$ | −61·1 | 127, 128 |
| $(NaO)_2P(O)OP(O)(ONa)_2$ | +6·0 | 127 |
| $(NaO)_2P(O)NHP(O)(ONa)_2$ | −2·7 | 127, 128 |
| | −2·5 | 22 |
| $(NaO)_2P(O)OP(O)(ONa)OP(O)(ONa)_2$ | +4, +18 | 127 |
| $(NaO)_2P(O)NHP(O)(ONa)NHP(O)(ONa)_2$ | −1·6 | 127, 128 |
|  O<br>ONa<br>P<br>β<br>HN<br>O<br>NaO<br>Pα<br>P<br>ONa<br>O<br>NH<br>β<br>O | +4·2 (α)<br>+7·9 (β) | 128 |
| $(NaO)_3(PONH)_3$ | +1·5 | 128 |
| $(KO)_4(PONH)_4$ | +3·7 | 128 |

* Relative to 85% phosphoric acid.

**Refs. p. 813**

From potentiometric titrations,[13] first and second ionization constants for monoamidophosphoric acid have been calculated. At 20°C. $K_1$ is $1{\cdot}19 \times 10^{-3}$ and $K_2$, $2{\cdot}10 \times 10^{-8}$. Other results given for these constants[83-4] are $K_1 = 2{\cdot}5 \times 10^{-5}$, $K_2 = 2{\cdot}0 \times 10^{-8}$ at 10°C. and $pK = 8{\cdot}2$ at 25°C.

## Chemical Properties

Monoamidophosphoric acid being dibasic[13] shows the characteristic double inflexion when titrated.

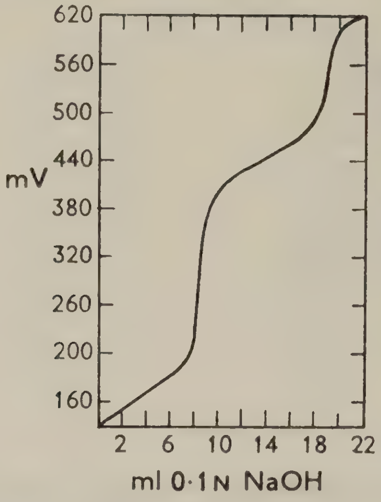


FIG. 3.—Potentiometric titration of monoamidophosphoric acid

The formation of zwitter-ions is consistent with the mechanism postulated for the hydrolysis of monoamidophosphates[17]:

$$HPO_3^-NH_3^+ + HOH \rightarrow H_2PO_4^- + NH_4^+$$

Chain extension can also occur by the following routes:

$$HPO_3^-NH_3^+ + H_2PO_4^- \rightarrow H_2P_2O_7^{2-} + NH_4^+$$
$$HPO_3^-NH_3^+ + H_2P_2O_7^{2-} \rightarrow H_2P_3O_{10}^{3-} + NH_4^+$$

although the probability of the last reaction taking place is low. The rate of hydrolysis[85] has been measured in media of various pH from 0·09 N. sodium hydroxide to 1·5 N. perchloric acid by following the formation of ammonia. The acid is not hydrolyzed in basic solution but below pH 7 the hydrolysis rate rises rapidly with decreasing pH. At pH 4 the rate is increased by added fluoride ion. The rates of hydrolysis of monoamidophosphoric acid are given in Table IV.

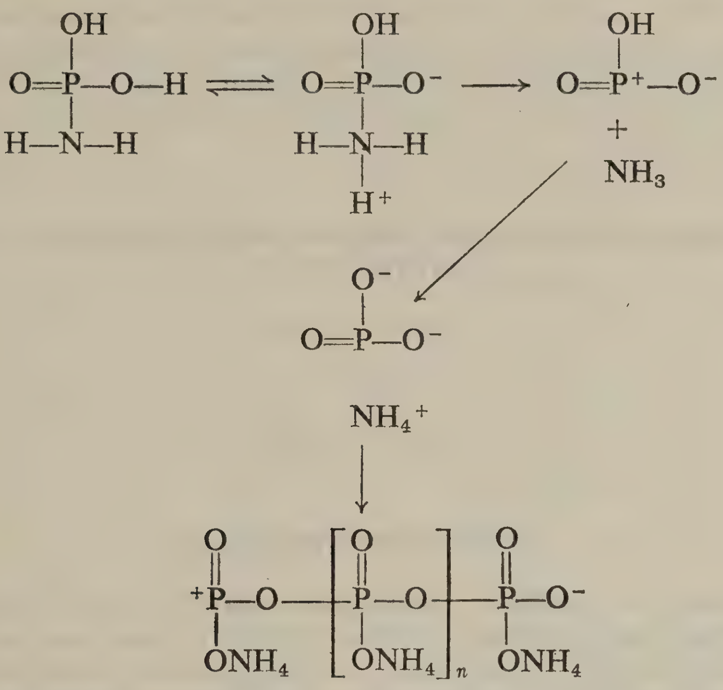
*Table IV.—Hydrolysis of Phosphoramidic Acid in* 0·217 M. $HClO_4$ *at various Temperatures*

| Temp. °C. | $10^4k$ (sec.$^{-1}$) | $\Delta E$ (kcal./mole) | $\Delta S$ (e.u.) |
|---|---|---|---|
| 10 | 0·79 | 16·8 | −14·06 |
| 25 | 3·28 | | |
| 35 | 8·35 | | |

The products of hydrolysis at pH 4·40 at 40·0°C. were examined by quenching[86] and examining the samples by ion exchange analysis. The hydrolysis was found to be a first-order reaction with $k = 3{\cdot}60 \times 10^{-2}$ min.$^{-1}$. During the course of the hydrolysis small quantities of pyrophosphate were detected. In the special case of monoammonium monoamidophosphate, hydrolysis gives rise to diammonium orthophosphate[13]:

$$NH_4HPO_3NH_2 + HOH \rightarrow (NH_4)_2HPO_4$$

A quantitative conversion of monoamidophosphoric acid to ammonium polyphosphate can be effected in 3 hr. at temperatures of 100–110°C., or more slowly at lower temperatures. The following intramolecular rearrangement[39] is envisaged:



Monoamidophosphates readily lose ammonia on heating, the extent of the loss depending on the temperature at which the deamination is conducted. These thermal decompositions are usually carried out *in vacuo*. At about 80°C. disodium monoamidophosphate hexahydrate loses its water only[18]:

$$Na_2PO_3NH_2,6H_2O \rightarrow Na_2PO_3NH_2 + 6H_2O$$

However, as the temperature is increased tetrasodium imidodiphosphate, hexasodium nitridotriphosphate and tetrasodium pyrophosphate are formed successively:

$$2Na_2PO_3NH_2 \xrightarrow[\text{in vacuo}]{210^\circ\text{C}} Na_4P_2O_6NH + NH_3{}^{18-9}$$

$$3Na_2PO_3NH_2 \xrightarrow[\text{in vacuo}]{450^\circ\text{C}} (Na_2PO_3)_3N + 2NH_3{}^{18}$$

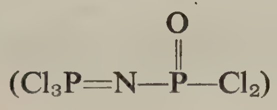
$$2Na_2PO_3NH_2 + H_2O \xrightarrow[\text{in air}]{1000^\circ\text{C}} Na_4P_2O_7 + 2NH_3{}^{20}$$

Slight variations in the reaction at 1000°C. are observed if the experiment is undertaken at a very low pressure in a quartz apparatus when, in addition to the pyrophosphate, reddish-brown materials having an odour of phosphine are produced.

An infra-red study of the decomposition of the potassium salt supported this mechanism.[129]

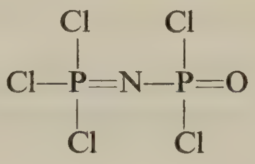
The acid reacts[87] with phosphorus pentachloride to give a crystalline product trichlorophosphonitridophosphoryl dichloride,

$P_2NOCl_5$



$$(Cl_3P{=}N{-}\overset{\overset{\large O}{\|}}{P}{-}Cl_2)$$

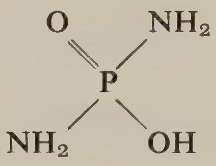
The structure of trichlorophosphonitridophosphoryl dichloride has been investigated by nuclear magnetic resonance,[88] the evidence supporting the structural formula:



$$\mathrm{Cl{-}PCl_2{=}N{-}PCl_2{=}O}$$

This product, which may also be formed by the reaction of phosphorus trichloride and dinitrogen tetroxide or phosphorus pentachloride and hydroxylamine salts,[87, 89-91] $P_2NOCl_5$, hydrolyzes in a restricted amount of acid to give monoamidophosphoric acid. In dilute alkali the hydrolysis product is the alkali salt of imidodiphosphoric acid.

## DIAMIDOPHOSPHORIC (PHOSPHORODIAMIDIC) ACID AND ITS SALTS



### Formation and Preparation

Although Stokes was unable to obtain pure crystalline alkali and alkaline earth diamidophosphates, his techniques (*Mellor*, VIII, 707) have been improved[24] and sodium diamidophosphate hexahydrate has been isolated after saponifying the phenyl ester. The hexahydrate, which can be readily dehydrated *in vacuo* at 80°C.,[18] has also been prepared by treating the silver salt, $AgPO_2(NH_2)_2$, with sodium bromide solution, removing the resultant silver bromide by filtration, and cooling the filtrate to −30°C. with simultaneous addition of ethyl alcohol. Similarly diamidophosphoric acid has been prepared from the silver salt and hydrobromic acid.[13] The acid is most readily prepared by catalytic hydrogenation of the phenyl ester[4] (cf. monoamidophosphoric acid).

Ammonolyses of halogen-containing compounds afford convenient preparative routes[25-6] for ammonium diamidophosphate. Thus a solution of pyrophosphoryl chloride in ether may, when treated with excess of ammonia in the presence of moisture, give the ammonium salt in yields between 85 and 92%. Polymeric phosphorus dioxychloride reacts with liquid ammonia almost quantitatively when maintained under pressure at room temperature for about 10 days:

$$(PO_2Cl)_x + 4xNH_3 \rightarrow xNH_4PO_2(NH_2)_2 + xNH_4Cl$$

In contrast with reactions which introduce amido groups into the molecule, it is possible to prepare diamidophosphates by eliminating an amido group from a compound containing three. Thus phosphoryl triamide is converted to sodium diamidophosphate by the action of warm 2 N. sodium hydroxide solution:

$$PO(NH_2)_3 + NaOH \rightarrow NaPO_2(NH_2)_2 + NH_3 \quad [13-4]$$

If acetone is added and the solution cooled to −30°C., sodium diamidophosphate tetrahydrate crystallizes.

## Physical Properties

Measurements of the conductivity of aqueous solutions of sodium diamidophosphates[13] have been made and corresponding values of the dissociation constant calculated for the acid:

| | 18°C. | 25°C. |
|---|---|---|
| Equivalent conductivity ($ohm^{-1}$ $cm.^2$) | 84·69 | 96·88 |
| Dissociation constant ($\times 10^{-5}$) | 1·20 | 1·49 |

Nuclear magnetic resonance spectra of aqueous solutions of the acid have been examined.[23] At 7140 gauss a chemical shift of $+3{\cdot}5$ p.p.m. is observed, relative to 85% orthophosphoric acid. Minor peaks occur at $+10$ and $+25$.

The infra-red spectrum of diamidophosphoric acid has been carefully examined.[30] Several assignments have been made and these are presented in Table V.

*Table V.—The Infra-red Spectrum of Diamidophosphoric Acid*

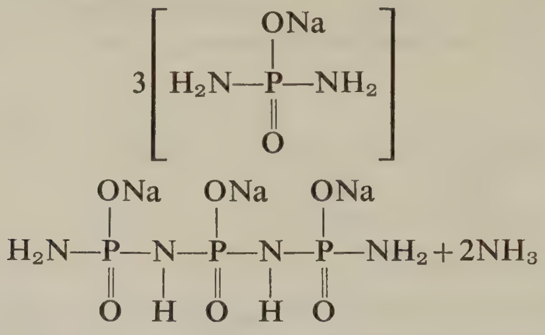
| Absorption frequency ($cm.^{-1}$) | Assignment |
|---|---|
| 3400 | as $NH_2$ |
| 3300 | s $NH_2$ |
| 2900 | as $NH_3$ |
| 2920 | |
| 2600 | s $NH_3$ |
| 2500 | |
| 1640 | as NH |
| 1620 | |
| 1460 | s $NH_3$ |
| 1200 | as $PO_2$ |
| 1000 | s $PO_2$ |
| 900 | PN |
| 700 | PN |
| 520 | s PO |
| 460 | as PO |

As with the monoamidophosphate ion the infra-red data provide evidence of zwitter-ion formation. The spectrum obtained from the zinc salt[21] is very similar to that observed[28] in the case of the lead salt.

## Chemical Properties

Free crystalline diamidophosphoric acid is not particularly stable, the action of moist air bringing about hydrolysis to ammonium monoamidophosphate[13]; if the crystals are dissolved in water this decomposition proceeds further to yield diammonium orthophosphate. Nevertheless the diamidophosphate ion is more stable than the monoamidophosphate[67] ion.

When a diamidophosphate or diamidophosphoric acid is heated, deamination tends to occur and gives rise to polymers containing P–N(H)–P bridges. The chain length of such polymers seems to depend on the temperature of reaction, higher temperatures being associated with higher molecular weights. At very high temperatures (*ca.* 900°C.) nitrogen can be completely eliminated from sodium diamidophosphate to give Graham's salt $(NaPO_3)_n$, provided that the heating is carried out in the presence of moist air.[20] An amorphous hygroscopic ammonium polyphosphimate results when diamidophosphoric acid is heated at 100°–110°C.[10] If sodium diamidophosphate is heated *in vacuo* to between 155° and 165°C., trisodium diamido-di-imidotriphosphate is obtained[18]:



$$3\left[\mathrm{H_2N{-}\overset{\displaystyle ONa}{\underset{\displaystyle O}{\overset{|}{\underset{\|}{P}}}}{-}NH_2}\right]$$

$$\mathrm{H_2N{-}\overset{\displaystyle ONa}{\underset{\displaystyle O}{\overset{|}{\underset{\|}{P}}}}{-}\underset{\displaystyle H}{\underset{|}{N}}{-}\overset{\displaystyle ONa}{\underset{\displaystyle O}{\overset{|}{\underset{\|}{P}}}}{-}\underset{\displaystyle H}{\underset{|}{N}}{-}\overset{\displaystyle ONa}{\underset{\displaystyle O}{\overset{|}{\underset{\|}{P}}}}{-}NH_2} + 2NH_3$$

More usually at these temperatures a mixture of homologues of general formula $Na_nP_nO_{2n}(NH)_{n-1}(NH_2)_2$ is formed[19]; at 200°C. $n$ is 6 and at 250°C. $n$ has a value in the region of 18.[24] An infra-red study of the decomposition of barium diamidophosphate confirmed these results, and showed that nitridotriphosphate does not occur among the decomposition products.[129]

The chemistry of the silver diamidophosphates has been reinvestigated[18] and the results differ from those reported by Stokes (*loc. cit.*). The monosilver salt is readily derived from the sodium salt or the free acid by precipitation with silver nitrate, under slightly acid or neutral conditions, respectively.[13] If the monosilver salt is treated with 30% potassium hydroxide, a potassium salt is obtained in which one of the hydrogen atoms in each of the amido groups is replaced by silver, i.e. $KPO_2(NHAg)_2,2H_2O$, which, when washed with boiling water, decomposes to a pentasilver salt, $AgPO_2(NAg_2)_2$:

$$5KPO_2(NHAg)_2 + 2H_2O \rightarrow 2AgPO_2(NAg_2)_2 + 3KPO_2(NH_2)_2 + 2KOH$$

Previously, the constitution of the pentasilver diamidophosphate was thought to be $(AgO)_3P(NHAg)_2$ (*Mellor*, VIII, 704), but on the basis of the evidence of analytical data, and of its reaction with methyl iodide in a sealed tube at 95°C.,

$$AgPO_2(NAg_2)_2 + 4CH_3I \rightarrow AgPO_2(N(CH_3)_2)_2 + 4AgI$$

in which only four of the silver atoms are replaced, the formula involving the disilver-substituted amido groups is preferred.

The pentasilver compound (*vide supra*), already known to undergo rapid spontaneous decomposition (*Mellor*, VIII, 705) has been shown to deposit metallic silver slowly if left for about a week.[13] Cleavage of the P–N bonds may also be effected by traces of rare-earth metal ions.[27] Thus at 37°C. and at pH 8·6 diamidophosphoric acid is decomposed by trivalent ions of cerium and lanthanum.

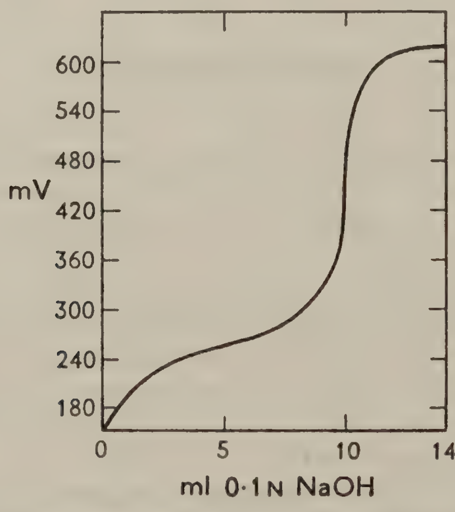
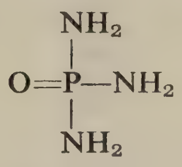


FIG. 4.—Potentiometric titration of diamidophosphoric acid

Diamidophosphoric acid titrates against decinormal alkali as a strong monobasic acid. Results obtained potentiometrically[13] show the neutral point to be at pH 8·5. Diamidophosphoric acid reacts with phosphorus pentachloride to give a crystalline compound, $P_2NOCl_7$ (see p. 481).[87]

## PHOSPHORYL TRIAMIDE



$$\begin{array}{ccc} & NH_2 & \\ & | & \\ O{=} & P & {-}NH_2 \\ & | & \\ & NH_2 & \end{array}$$

### Preparation

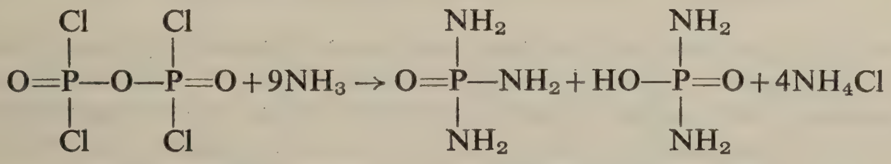
The amination of phosphoryl trichloride was formerly considered a somewhat doubtful preparative technique (*Mellor*, VIII, 707). However, 94% yields of phosphoryl triamide have been obtained[32] by treating phosphoryl trichloride with liquid ammonia,

$$POCl_3 + 6NH_3 \rightarrow PO(NH_2)_3 + 3NH_4Cl$$

or alternatively by passing gaseous ammonia into a solution of phosphoryl trichloride in chloroform at −10°C. and refluxing the precipitate with a mixture of diethylamine and chloroform to free it from ammonium chloride.[14] Reaction of phosphorus pentachloride with ammonia[40] and water according to the equation:

$$PCl_5 + 8NH_3 + H_2O \rightarrow O{=}P(NH_2)_3 + 5NH_4Cl$$

gives a good yield of phosphoryl triamide. The amide may be recrystallized from methyl alcohol. Condensed phosphoryl chlorides behave similarly[25] yielding condensed phosphoryl amides but, if the reaction is allowed to take place in the presence of excess of ammonia and some moisture, phosphoryl triamide usually occurs among the other products, e.g.:



$$\begin{array}{ccccccccc} & Cl & & Cl & & & NH_2 & & NH_2 & \\ & | & & | & & & | & & | & \\ O{=} & P & {-}O{-} & P & {=}O + 9NH_3 \rightarrow O{=} & & P & {-}NH_2 + HO{-} & P & {=}O + 4NH_4Cl \\ & | & & | & & & | & & | & \\ & Cl & & Cl & & & NH_2 & & NH_2 & \end{array}$$

If phosphorus pentachloride is treated with ammonia, an intermediate of indeterminate composition, possibly phosphorimidyl triamide, is formed, which hydrolyzes to phosphoryl triamide[33,40]:

$$PCl_5 + 9NH_3 \rightarrow NH{:}P(NH_2)_3 + 5NH_4Cl$$
$$NH{:}P(NH_2)_3 + H_2O \rightarrow O{:}P(NH_2)_3 + NH_3$$

### Physical Properties

This compound is slightly soluble in absolute methanol (0·7 g. per 100 ml. at 20°C.) but virtually insoluble in other common solvents, e.g. pyridine, nitrobenzene, acetone, ether, chloroform and ethanol.[67]

Infra-red and Raman spectra have been examined,[21,30,92,130] the peaks and their assignments being listed in Table VI. The assignments are compatible with $C_{3v}$ symmetry for the molecule.[130]

The solution in water is neutral (pH = 6), the low specific conductivity of a 0·1 M. solution at 20°C., viz. $10^{-4}$ ohm$^{-1}$ cm.$^{-1}$, indicating little ionization under these conditions.[67]

*Table VI.—The Infra-red and Raman Spectra of Phosphoryl Triamide*

| Raman frequencies (aqueous solution) | Infra-red frequencies (in potassium bromide) | Assignment |
|---|---|---|
| | 3390 cm, $^{-1}$ | $\nu_{as}$NH |
| | 3280 | $\nu_s$NH |
| 1623 cm.$^{-1}$ | 1625 | $\delta$NH$_2$ E |
| 1560 | 1590 | $\delta$NH$_2$ A$_1$ |
| 1174 (medium) | 1200 | $\nu$PO A$_1$ |
| 1001 (weak) | 1050 | $\rho$NH$_2$ E+A$_1$ |
| 928 (weak) | 955 | $\omega$NH$_2$ E |
| 832 (strong) | — | $\nu_s$PN A$_1$ |
| 700 (?) | 725 | $\nu_{as}$PN E |
| 604 (?) | 615 | $\delta$PO E |
| 455 (medium) | 460 | $\delta_s$PN A$_1$ |
| 309 (weak) | — | $\delta_{as}$PN E |

## Chemical Properties

Phosphoryl triamide is a fairly stable compound when dry, but if exposed for several weeks to a damp atmosphere it hydrolyzes to ammonium monoamidophosphate. If it is heated on a water-bath with dilute sodium hydroxide solution, monosodium diamidophosphate is produced[14]:

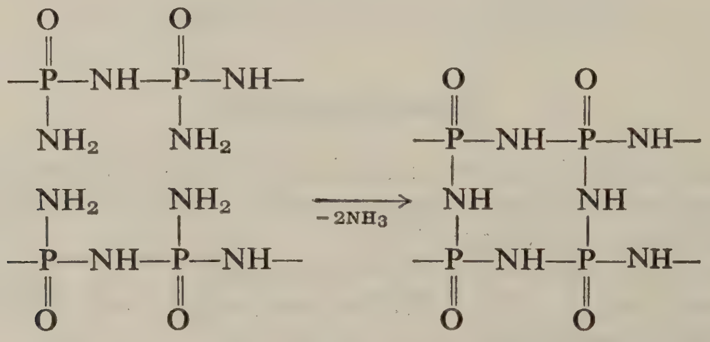
$$PO(NH_2)_3 + NaOH \rightarrow NaPO_2(NH_2)_2 + NH_3$$

As with many compounds containing P–N bonds, there is a marked tendency for self-condensation to occur, resulting in larger molecules. Thus condensed materials of the general formula $P_nO_n(NH)_{n-1}(NH_2)_{n+2}$ are formed by boiling a suspension of phosphoryl triamide in an organic medium such as benzene or toluene. The value of $n$ varies between 2 and 5[20]:

$$2PO(NH_2)_3 \rightarrow NH_3 + (NH_2)_2PO(NH)PO(NH_2)_2, \quad \text{etc.}$$

Water-soluble products of this type have been separated by paper chromatography.[20] When heated to 180°C. phosphoryl amide[93–4, 130–1] condenses rapidly to form phosphoryl imidoamide which is relatively stable at this temperature. The reaction is of at least second order, giving a polymeric product. The reaction–time curve is shown in Fig. 5 and the graph for third-order kinetics in Fig. 6.

Further heating results in the polymer cross-linking to form a product with the empirical formula $P_2O_2N_3H_3$. A temperature of 300°C. was required to give rapid cross-linking (see Fig. 5). The amount of ammonia evolved suggested a condensation of the type:



This polymer is a white amorphous powder insoluble in water and fairly resistant to hydrolysis. It is stable at 300°C., and temperatures of the order of 600°C. are required to convert it to phosphorus oxynitride P≡N=O.

The mechanism of these condensation reactions usually involves the elimination of ammonia. Hence the addition of a suitable reagent such as dry hydrogen chloride, to combine with the ammonia, favours the process.[19, 34] The chain length of the products depends upon the temperature and the concentration of the hydrogen chloride in the inert medium in which the reagents are suspended or dissolved. When hydrogen chloride is passed into a solution of phosphoryl triamide in diethyl ether for a period of 3 hr. at a temperature of −15°C. the dimer is obtained, in 100% yield, whilst at about 30°C. the passage of hydrogen chloride for 4 hr. gives the trimer in 86% yield.[35]

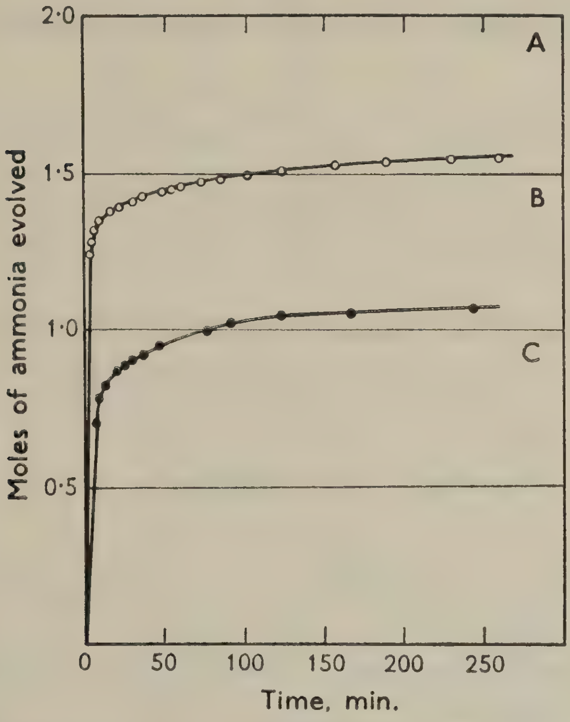


FIG. 5.—Condensation of phosphoramide at 180° (○) and 300° (●)
A theory for linear polymer $(PON_4H_3)_n$
B theory for cross-linked polymer $(P_2O_2N_3H_3)_n$
C theory for $(PON)_n$

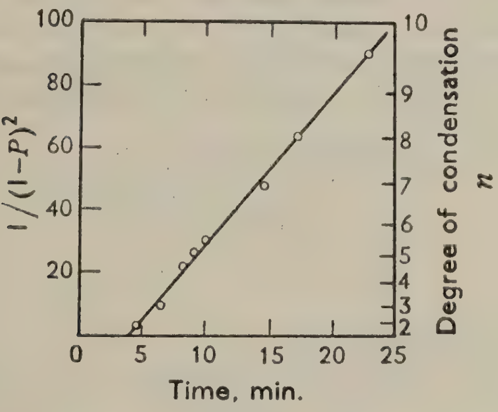
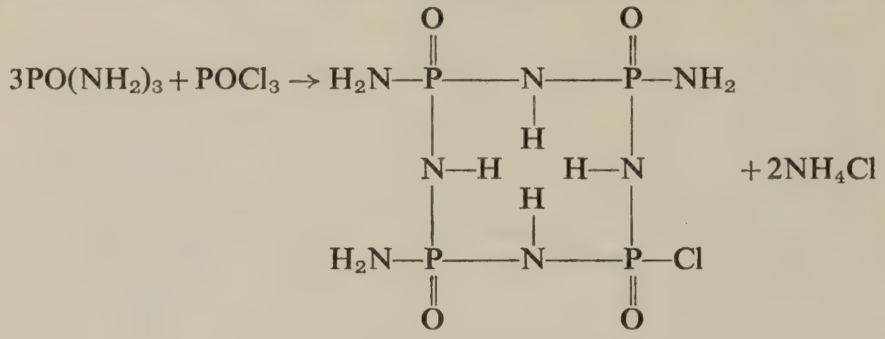
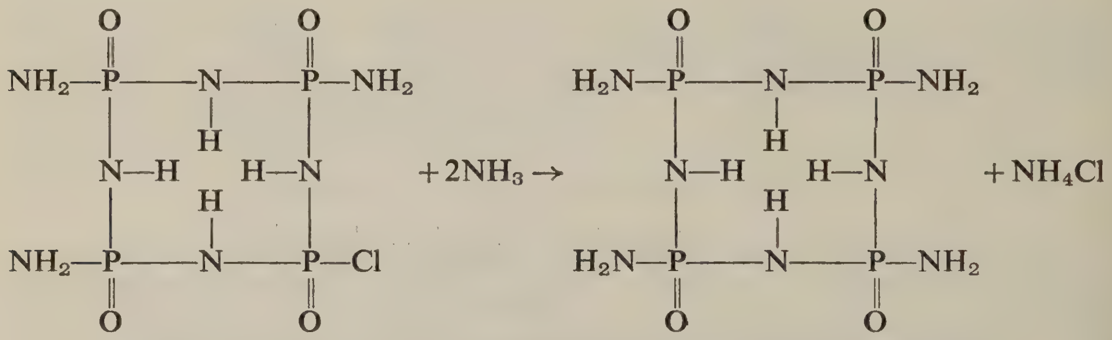


FIG. 6.—Condensation of phosphoramide at 180° plot of $1/(1-P)^2$ against time for third-order kinetics
$P$ = mole fraction reacted

A similar reaction occurs in the presence of phosphoryl trichloride. Phosphoryl triamide and phosphoryl trichloride when shaken together for 3 hr. in the cold yield a precipitate which when filtered off under dry nitrogen, washed with chloroform, liquid ammonia and finally water, gives polyphosphoryl polyamide. However, by dissolving the precipitate in formamide and adding acetone, an intermediate, possibly tetrametaphosphimic chloride triamide, has been isolated,[57] although its constitution is uncertain:

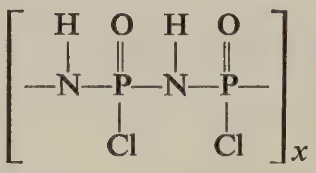


The action of liquid ammonia removes the ammonium chloride and ammonolyzes the chlorine atom:



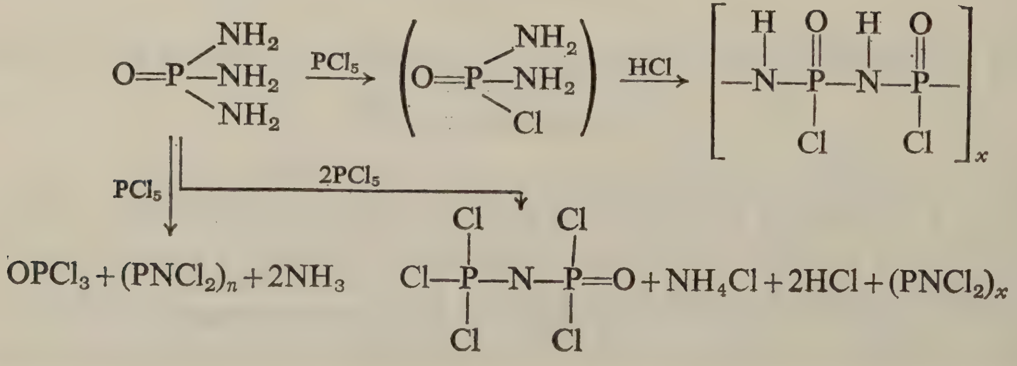
However, the tetrametaphosphimic tetramide has not been isolated, the final product being an amorphous polymer, $(HNPONH_2)_n$.

It seems very likely that this capacity for self-condensation has led to the adoption of phosphoryl triamide as a flame retardant for various combustible materials, including paint, textiles and wood.[36-8, 95-7] Phosphoryl triamide reacts[87] with phosphorus pentachloride to give a mixture consisting of a crystalline compound of the formula $P_2NOCl_5$ (see p. 481), phosphonitrilic chlorides and a polymer



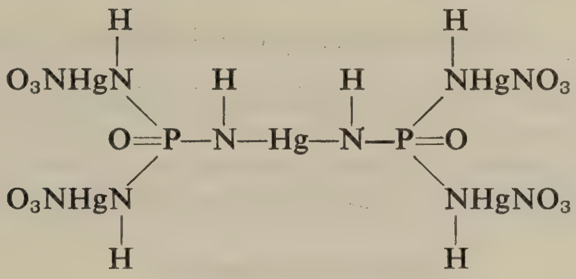
$$\left[-\overset{H}{N}-\underset{Cl}{\overset{O}{P}}-\overset{H}{N}-\underset{Cl}{\overset{O}{P}}-\right]_x$$

the possible reaction paths being:

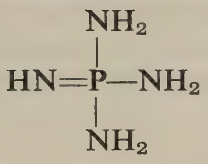


The electrochemical fluorination of phosphoryl triamide in hydrogen fluoride yielded $OF_2$, $N_2$, $N_2O$ and $NF_3$. The same products, with the exception of oxygen difluoride, were formed from phosphorimidyl triamide (see below). In neither case could volatile phosphorus compounds be detected in the products.[132]

From a methanolic solution of phosphoryl triamide, silver nitrate precipitates a complex $[(PO(NH_2)_3)Ag]NO_3$ as silky leaflets, whilst in aqueous solution mercuric nitrate yields an insoluble white flocculent compound $Hg_5[(PO(NH)_3)_2(NO_3)_4]$, which is not a complex but a genuine amidate represented by the structure[14]:



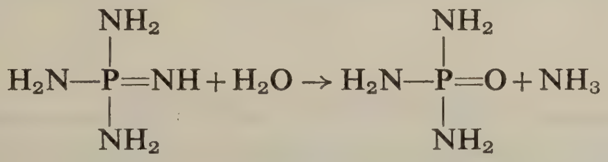
## PHOSPHORIMIDYL TRIAMIDE



$$\mathrm{HN{=}\overset{NH_2}{\underset{NH_2}{P}}{-}NH_2}$$

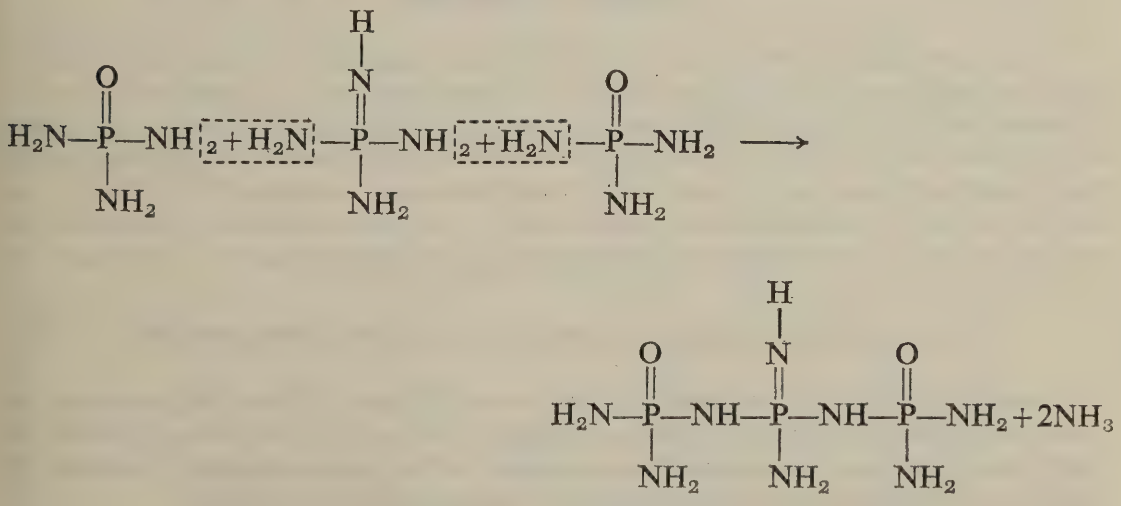
This compound has been postulated as an intermediate in the reaction of phosphorus pentachloride with ammonia.[33] Other authorities differ[54–6] but the existence of such an intermediate would satisfactorily explain the subsequent formation of phosphoryl triamide, tri-imidotriphosphoric pentamide and polyammonium polyimidopolyphosphate, as the reaction conditions varied.

Assuming phosphorimidyl triamide were produced, the action of moisture would most probably give rise to phosphoryl triamide:



$$\mathrm{H_2N{-}\overset{NH_2}{\underset{NH_2}{P}}{=}NH + H_2O \rightarrow H_2N{-}\overset{NH_2}{\underset{NH_2}{P}}{=}O + NH_3}$$

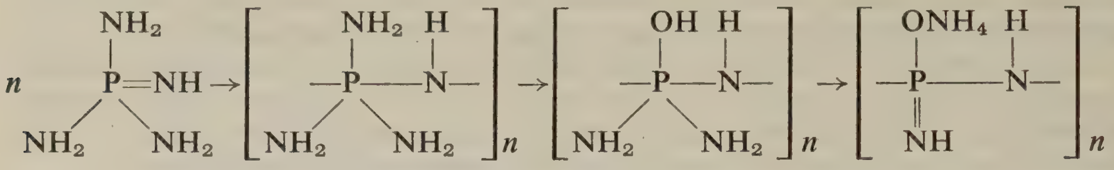
Furthermore the formation of tri-imidotriphosphoric pentamide is adequately explained by considering the deamination of 2 molecules of phosphoryl triamide and one molecule of phosphorimidyl triamide:



$$\mathrm{H_2N{-}\overset{O}{\overset{\|}{\underset{NH_2}{P}}}{-}NH\boxed{_2+H_2N}{-}\overset{\overset{H}{|}}{\overset{N}{\overset{\|}{\underset{NH_2}{P}}}}{-}NH\boxed{_2+H_2N}{-}\overset{O}{\overset{\|}{\underset{NH_2}{P}}}{-}NH_2 \longrightarrow}$$

$$\mathrm{H_2N{-}\overset{O}{\overset{\|}{\underset{NH_2}{P}}}{-}NH{-}\overset{\overset{H}{|}}{\overset{N}{\overset{\|}{\underset{NH_2}{P}}}}{-}NH{-}\overset{O}{\overset{\|}{\underset{NH_2}{P}}}{-}NH_2 + 2NH_3}$$

The following mechanism has been suggested for the formation of polyammonium polyimidopolyphosphate:

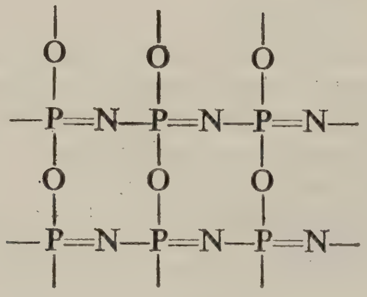


## PHOSPHORUS OXYNITRIDE

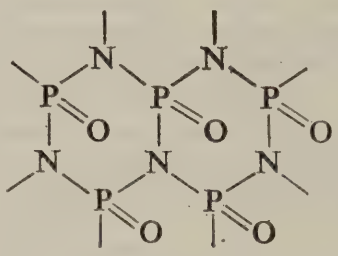
Phosphorus oxynitride, $(PON)_x$, is obtained by heating phosphoryl imidoamide to red-heat[98-100] in the absence of air. The material was at first thought to be monomeric but Oddo[101] suggested a dimeric structure to account for its stability. The true molecular weight must, however, be very much higher than this.

### Physical Properties

The compound[93] is an involatile white powder which melts above 1000°C. to form a glass. The glass exists in at least three forms: opaque, crystalline-transparent and black. The powder is amorphous to *X*-rays but shows two wide absorption bands in the infra-red at 900–1050 cm.$^{-1}$ and 1200–1400 cm.$^{-1}$ Two possible basic structures are:



I



II

The former is supported by the similarity between the oxynitride and the reaction product of polyphosphonitrilic compounds and metal oxides. The similar properties of the oxynitride and silica also suggest that their structures are isoelectronic which would be the case with structure I.

### Chemical Properties

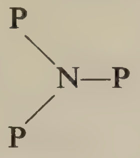
At low pressures above 750°C.[102] phosphorus oxynitride decomposes slowly to give phosphorus pentoxide, phosphorus nitride and nitrogen. It is insoluble in normal solvents and is not attacked by aqueous dilute acids and alkalis. Fusion with alkalis decomposes the oxynitride to give ammonia and the alkali metal phosphate. Concentrated sulphuric acid decomposes it to give ammonium phosphate. Water hydrolyzes the oxynitride[103] at temperatures above 200°C. to give ammonium phosphate and phosphoric acid. Further data on this compound are given in Section VIII (page 371).

## POLYPHOSPHORIC ACIDS CONTAINING P–N BONDS

Several possibilities arise depending on the environment of the nitrogen atoms in a particular molecule. Amido, imido and nitrido derivatives are distinguishable. So many permutations and combinations are possible that, understandably, no coherent pattern of the chemistry of these compounds seems to have emerged.

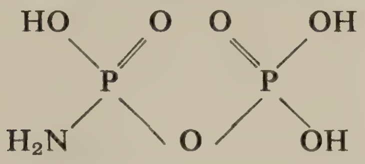
The category above therefore includes the following:

(*a*) Straight chains containing P–O–P or P–N(H)–P bridges or both.
(*b*) Branched chains containing



forks and bridges as indicated above.
(*c*) Any combination of P–$NH_2$ groupings with the bridges and forks together with the rare occurrence of P=NH groupings.

## MONOAMIDODIPHOSPHORIC ACID



By treating phosphorus pentoxide with ammonia under various conditions, the diammonium and triammonium salts of this acid have been prepared.[41] The action of gaseous ammonia on solid phosphorus pentoxide, phosphorus pentoxide suspended in an inert liquid or phosphorus pentoxide prepared *in situ* by burning red phosphorus in oxygen, yielded diammonium monoamidodiphosphate, which on further ammoniation was converted to triammonium monoamidodiphosphate:

$$P_2O_5 + 3NH_3 + H_2O \rightarrow (NH_4)_2HP_2O_6NH_2$$
$$(NH_4)_2HP_2O_6NH_2 + NH_3 \rightarrow (NH_4)_3P_2O_6NH_2$$

By increasing the humidity it was possible to improve the yields in these reactions.

### Physical and Chemical Properties

Both the di- and tri-ammonium amidodiphosphates are hygroscopic and soluble in water.

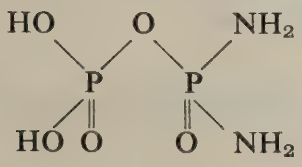
The above two salts are alkaline to methyl orange, but although the former is acid to phenolphthalein, the latter seems neutral.

Even at ambient temperature the amidodiphosphate ion decomposes in aqueous solution to orthophosphate. At boiling temperature or in the presence of a mineral acid such decomposition is accelerated.

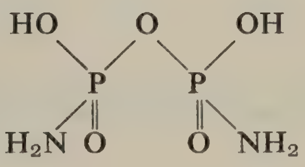
If the salts are heated in an inert gas stream, they lose most of their nitrogen, gradually turn yellow, then red, melt at about 260°C., and subsequently solidify to a glassy mass.

## DIAMIDODIPHOSPHORIC ACID

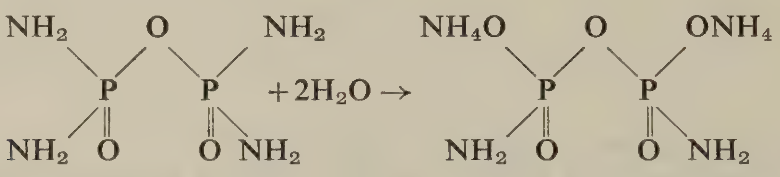
Two isomers are possible:



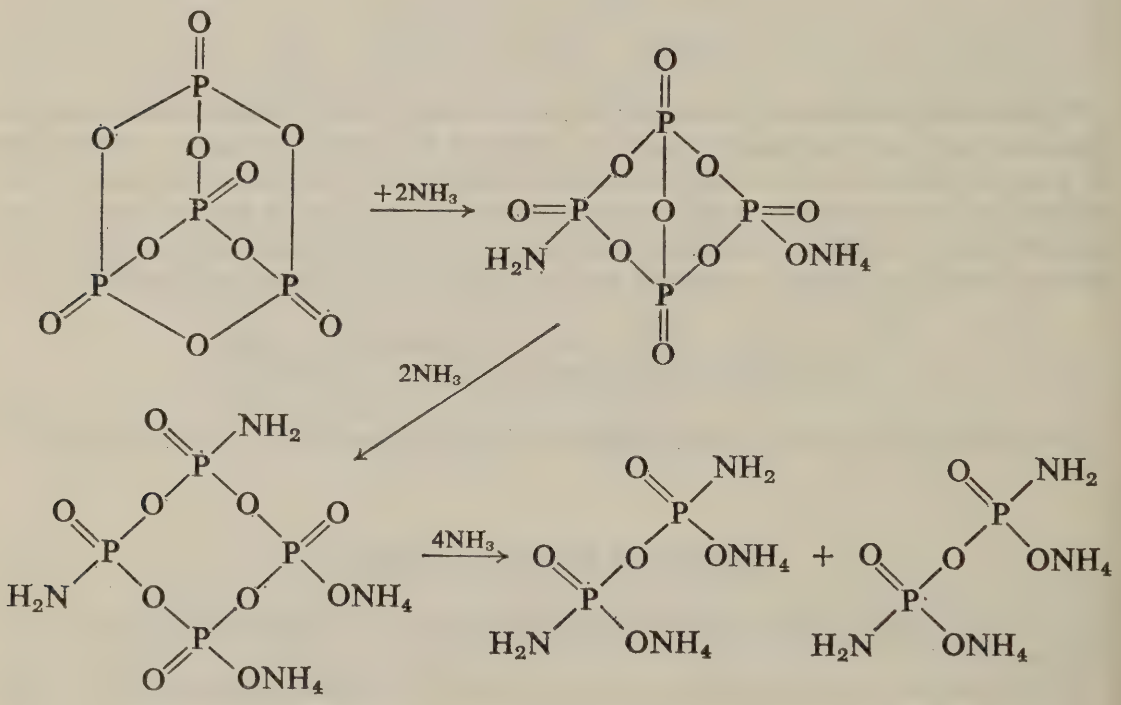
and



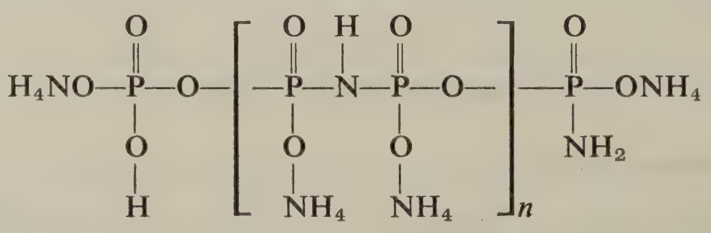
Previously (*Mellor*, VIII, 710) no attempt had been made to distinguish between these alternatives. However, when the diammonium salt was isolated from a solution of pyrophosphoryl tetramide by the addition of acetone and subsequent desiccation of the resultant oil, it was regarded[42] as the symmetrical form:



It has been claimed[10] that diammonium diamidodiphosphate can also be prepared by leaving a mixture of phosphorus pentoxide and excess of liquid ammonia in a sealed tube at room temperature for 5 or 6 weeks. The following mechanism has been suggested:

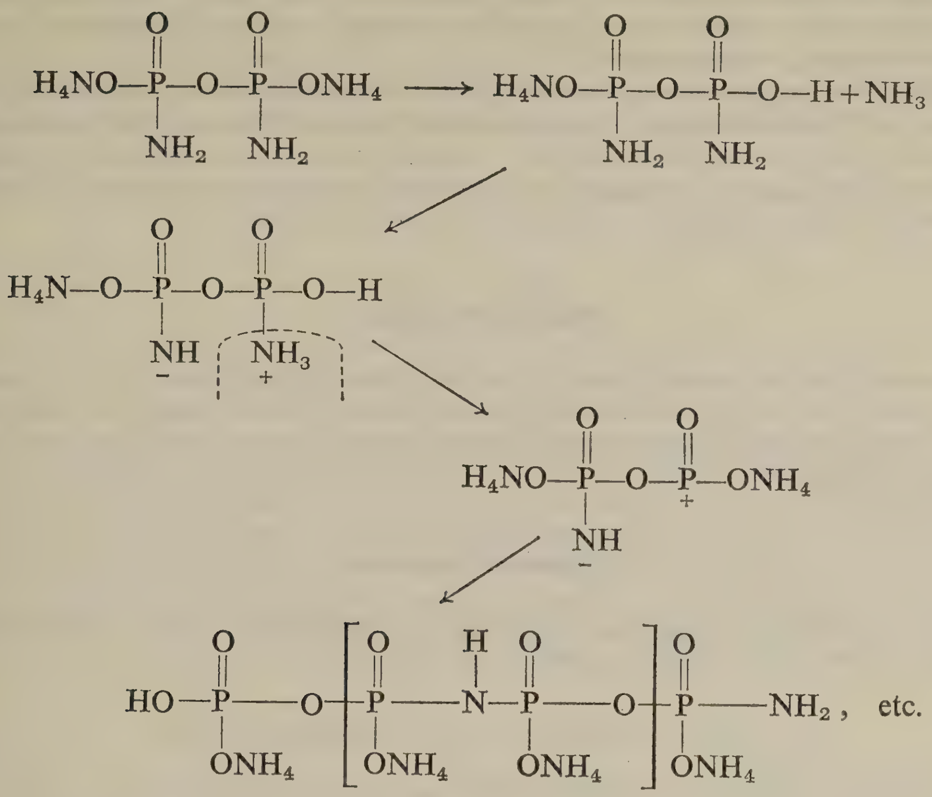


If this compound, together with any co-products, is heated, a chain compound is obtained containing both P–$\underset{\underset{H}{|}}{N}$–P and P–O–P bridges:

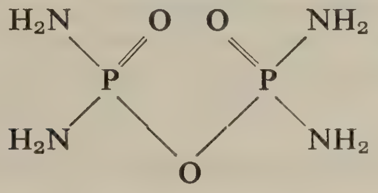


$$H_4NO{-}\underset{\underset{\displaystyle H}{\overset{|}{O}}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O{-}\left[{-}\underset{\underset{\displaystyle NH_4}{\overset{|}{O}}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\underset{\underset{\displaystyle NH_4}{\overset{|}{O}}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O{-}\right]_n{-}\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}ONH_4$$

where *n* is about 4. To explain this reaction the following mechanism has been postulated:

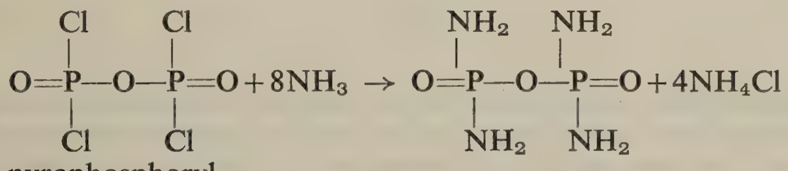


## PYROPHOSPHORYL TETRAMIDE



### Formation and Preparation

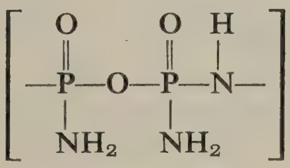
The application of the general method of aminating the appropriate chloro-derivative has proved successful:



$$O{=}\underset{Cl}{\overset{Cl}{P}}{-}O{-}\underset{Cl}{\overset{Cl}{P}}{=}O+8NH_3 \rightarrow O{=}\underset{NH_2}{\overset{NH_2}{P}}{-}O{-}\underset{NH_2}{\overset{NH_2}{P}}{=}O+4NH_4Cl$$

pyrophosphoryl chloride

By treating pyrophosphoryl chloride with liquid ammonia, 89% yields were obtained.[35] However, an intermediate polymeric form tends to appear[25, 43, 133-4] containing



$$\left[-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{NH_2}{\overset{O}{\overset{\|}{P}}}{-}\overset{H}{N}-\right]$$

units, which needs to be further treated with liquid ammonia to obtain pyrophosphoryl tetramide in a pure state. Diamidophosphoric acid and phosphoryl triamide are also observed as by-products.[134]

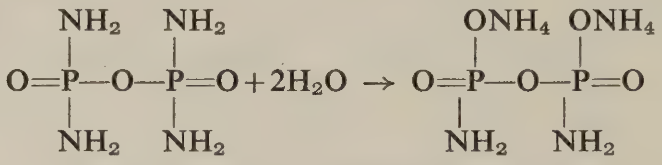
The reaction has also been effected by dissolving each of the reactants in chloroform, and adding the solution of pyrophosphoryl chloride dropwise to the ammoniacal solution in a vessel cooled to 0°C. The ammonium chloride was removed by extraction with liquid ammonia,[42] or better with cold absolute alcohol,[134] resulting in an overall yield of 74%.

## Physical Properties

Pyrophosphoryl tetramide forms colourless, odourless, hygroscopic crystals which are reported[42] to have a sweet taste. It is insoluble in most organic solvents. In the presence of ammonia it is sparingly soluble in water. It is also only sparingly soluble in liquid ammonia.[43]

## Chemical Properties

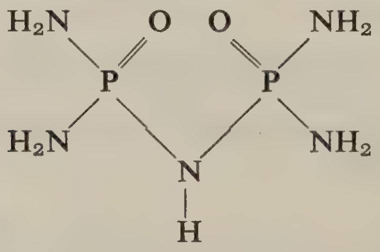
It is impossible[42] to dissolve pyrophosphoryl tetramide in water without decomposition of two of the amido groups to ammonium ions:



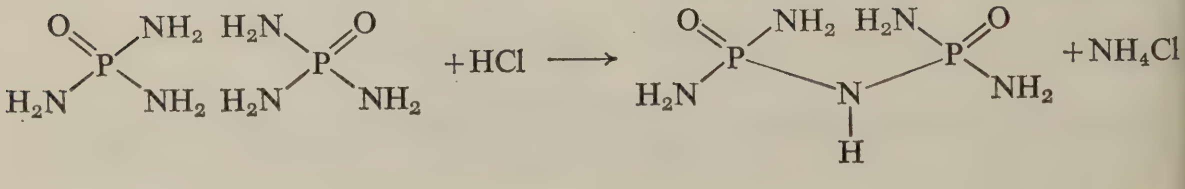
$$O{=}\overset{NH_2}{\underset{NH_2}{P}}{-}O{-}\overset{NH_2}{\underset{NH_2}{P}}{=}O + 2H_2O \rightarrow O{=}\overset{ONH_4}{\underset{NH_2}{P}}{-}O{-}\overset{ONH_4}{\underset{NH_2}{P}}{=}O$$

thus yielding diammonium diamidodiphosphate (*q.v.*). The thermal decomposition of pyrophosphoryl tetramide alone, or in xylene, at 300°–600°C. gives products of lower N:P ratios which contain P–NH–P bonds but no $P{-}N{=}(P)_2$ groups.[134]

## PYROPHOSPHORIMIDYL TETRAMIDE

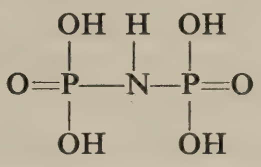


This compound has been obtained by an anionic deamination technique.[19] Dry hydrogen chloride was passed into a suspension of phosphoryl triamide in ether at −15°C. After 3 hr. the mixture of ammonium chloride with pyrophosphorimidyl tetramide (or imidodiphosphoric acid tetramide) was treated with liquid ammonia. This process removed the ammonium chloride, leaving white crystals, easily soluble in water[35]:



A 0·03 M. solution has pH of 4·3 at 35°C., but on standing for 25 hr. this rises to 6·85 because of hydrolytic decomposition. The addition of sodium hydroxide brings about the evolution of 2 moles of ammonia per mole of pyrophosphorimidyl tetramide. The diffraction pattern obtained by *X*-ray powder photography bears a striking resemblance to that obtained from pyrophosphoryl tetramide.[42]

## IMIDODIPHOSPHORIC ACID

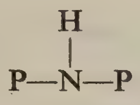


$$O{=}P(OH)_2{-}N(H){-}P(OH)_2{=}O$$

Of the imidodiphosphoric acids mentioned before (*Mellor*, VIII, 712), only the tetra-basic acid seems plausible. All other possibilities involve four-membered rings which, from general stereochemical considerations, seem unlikely to remain stable. Furthermore, three of the hypothetical acids which were described were thought to be identical with mono-, di- and tri-amidodiphosphoric acids (*loc. cit.*) and in the light of their properties and more recent data this view seems correct.

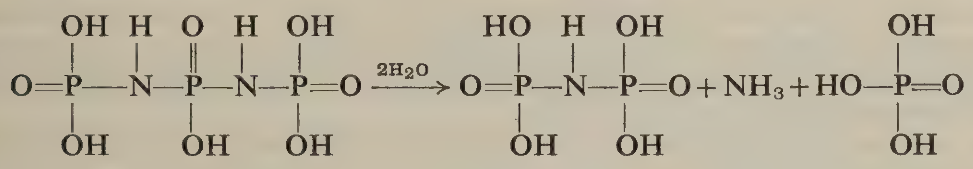
### Formation and Preparation

Imidodiphosphates tend to occur as minor components in the hydrolysates of larger molecules or ions containing the

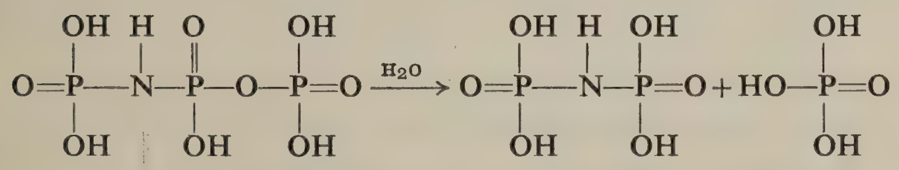


$$P{-}N(H){-}P$$

grouping, e.g. trimetaphosphimates (*Mellor*, VIII, 712), di-imidotriphosphates[17, 45–6] and monoimidotriphosphates[17, 46]:



$$O{=}P(OH)_2{-}N(H){-}P(O)(OH){-}N(H){-}P(OH)_2{=}O \xrightarrow{2H_2O} O{=}P(OH)_2{-}N(H){-}P(OH)_2{=}O + NH_3 + HO{-}P(OH)_2{=}O$$



$$O{=}P(OH)_2{-}N(H){-}P(O)(OH){-}O{-}P(OH)_2{=}O \xrightarrow{H_2O} O{=}P(OH)_2{-}N(H){-}P(OH)_2{=}O + HO{-}P(OH)_2{=}O$$

Degradative reactions of this type are not particularly convenient preparative techniques. However, condensation of two smaller molecules with the elimination of ammonia[12, 18–9, 24] provides a useful device for obtaining good yields of the salts:

$$2Na_2PO_3NH_2 \rightarrow Na_4P_2O_6NH + NH_3$$
$$2Ag_2PO_3NH_2 \rightarrow Ag_4P_2O_6NH + NH_3$$

It is necessary to carry out these reactions *in vacuo* under controlled conditions as the degree of condensation seems to depend on the temperature. Thus tetrasodium imidodiphosphate was obtained by heating disodium amidophosphate for 7 days *in vacuo* at 210°C. The yield is reported to be improved by the addition of a fluxing agent such as an alkali metal formate or phenoxide.

There have been obtained 95% yields of tetrasodium imidodiphosphate by saponifying a diphenyl ester with excess of sodium hydroxide and phenol under reflux at 135°C. for 15 min.[22] though the presence of the latter does not seem essential.[104] Lower yields were obtained when the reaction took place under pressure in the absence of phenol. The technique is claimed to be applicable to the preparation of any of the alkali metal salts.

The free acid, which Stokes (*Mellor*, VIII, 713) was unable to prepare, has been made by treating an aqueous solution of the tetrasodium salt with the hydrogen form of a cation exchange resin, although it could not be obtained solid.[12, 22]

Tetrathallium imidodiphosphate was obtained by neutralization[22]:

$$H_4P_2O_6NH + 4TlOH \rightarrow Tl_4P_2O_6NH + 4H_2O$$

but most salts can be prepared by metathesis. Soluble salts like tetrapotassium and tetrammonium imidodiphosphates were isolated by treating the silver salt with the appropriate sulphide.

Acid salts arise when the pH of solutions of the normal salts is lowered by the addition of acetic acid:

$$K_4P_2O_6NH + 2HOAc \rightarrow K_2H_2P_2O_6NH + 2KOAc$$
$$(NH_4)_4P_2O_6NH + 2HOAc \rightarrow (NH_4)_2P_2O_6NH + 2NH_4OAc$$

The tetrammonium salt which occurs as a trihydrate loses both water and ammonia in the atmosphere to give triammonium imidodiphosphate with 1·5 molecules of water of crystallization:

$$(NH_4)_4P_2O_6NH,3H_2O \rightarrow (NH_4)_3HP_2O_6NH,1{\cdot}5H_2O + NH_3 + 1{\cdot}5H_2O$$

## Physical Properties

The imidodiphosphates tend to resemble the pyrophosphates. Thus *X*-ray diffraction data[12, 18] indicate that tetrasodium imidodiphosphate decahydrate and tetrasodium pyrophosphate decahydrate are isomorphous. However, sodium imidodiphosphate is rather more soluble than the pyrophosphate, the solubilities of the decahydrates at 25°C. being 34·8 and 11·6 g./100 ml. of water respectively.[22]

Measurements of nuclear magnetic resonance spectra of tetrasodium imidodiphosphate at a frequency of 16·192 Mc. indicated a chemical shift of −2·5 p.p.m. of the applied field with respect to 85% phosphoric acid. The chemical shift for tetrasodium pyrophosphate was +5·5 p.p.m.

The infra-red spectra of several imidodiphosphates have been examined,[21] including the normal sodium, potassium, zinc and thallium salts, together with the dihydrogen dipotassium salt and its deuterated analogue. Typical assignments are presented in Table VII.

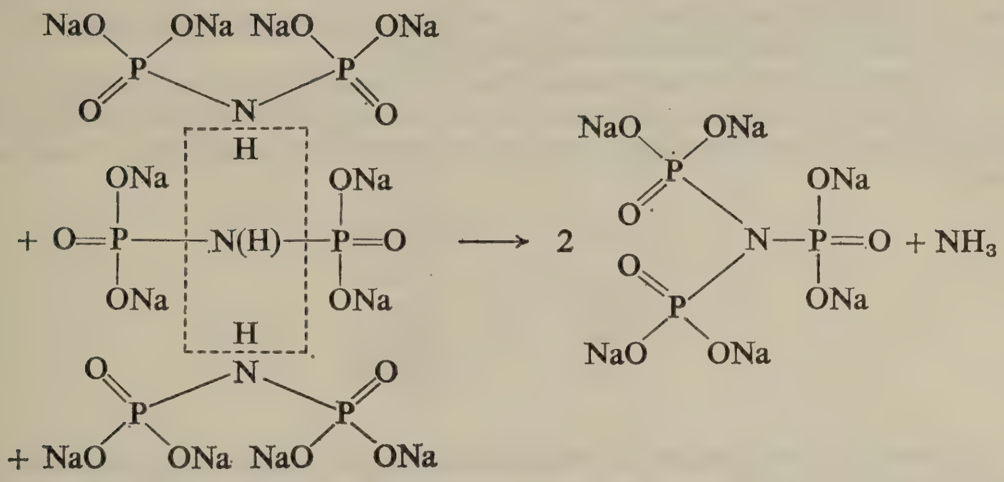
*Table VII.—Infra-red Absorption Spectra of Imidodiphosphates*

| Frequency range (cm.$^{-1}$) | Assignment |
|---|---|
| 3200–2900 | $\rangle$N—H* stretching |
| *c.* 2350 | $\rangle$N—D stretching |
| 2700–2560 | P—OH |

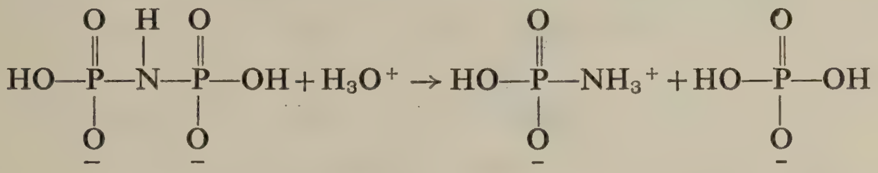
*The pentasilver salt does not contain an N–H bond and this frequency is therefore absent.

## Chemical Properties

The deamination procedure used to prepare imidodiphosphates need not stop at this point. Thus if tetrasodium imidodiphosphate is heated *in vacuo* at a temperature of 450°C., further loss of ammonia takes place to yield hexasodium nitridotriphosphate:

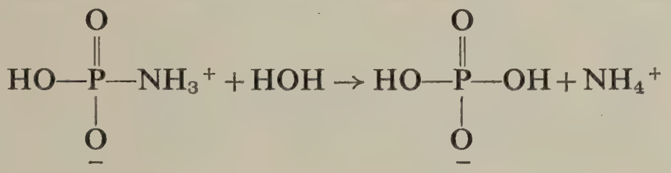


The hydrolysis of condensed imidophosphoric acids has been studied in detail.[17, 46] Very plausible mechanisms have been suggested. A hydroxonium ion may approach the —NH group and bring about fission at this point:

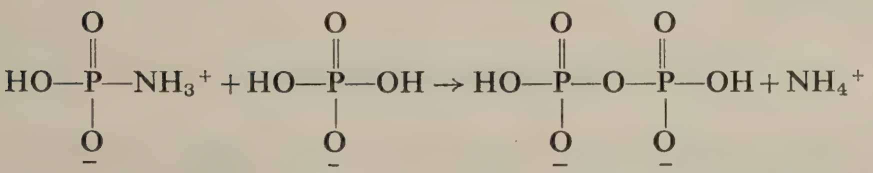


$$\mathrm{HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-\overset{\overset{H}{|}}{N}-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-OH + H_3O^+ \rightarrow HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-NH_3{}^+ + HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-OH}$$

The amidophosphate thus produced may be decomposed by water to orthophosphate and ammonium ions, or alternatively may eject an ammonium ion and recombine with an orthophosphate residue resulting in a pyrophosphate ion:



$$\mathrm{HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-NH_3{}^+ + HOH \rightarrow HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-OH + NH_4{}^+}$$



$$\mathrm{HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-NH_3{}^+ + HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-OH \rightarrow HO-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-OH + NH_4{}^+}$$

This scheme would satisfactorily account for several reactions that have been observed.[12]

Thus silver imidodiphosphate hydrolyses to pyrophosphate:

$$Ag_4P_2O_6NH + H_2O \rightarrow Ag_4P_2O_7 + NH_3$$

and sodium imidodiphosphate decomposes to monoamidophosphate and orthophosphate:

$$Na_4P_2O_6NH + H_2O \rightarrow Na_2PO_3NH_2 + Na_2HPO_4$$

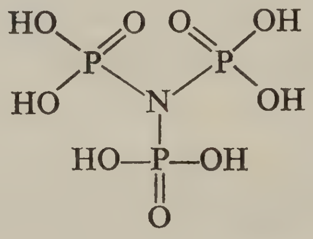
Analysis[86] by ion exchange chromatography of quenched samples from the hydrolysis at pH 4·40 and 40·0°C. showed that the reaction was first order with $k \sim 10^{-1}$ min.$^{-1}$. A small amount of pyrophosphate was also detected. The free acid decomposes similarly although there is also a tendency for the amidophosphate to break down further to orthophosphate and ammonia.

The reaction giving rise to pyrophosphate is slow and that to orthophosphate more rapid. However, in general the rate of decomposition is dependent upon the pH.[17] Tabulated below are the quarter lives of the imidodiphosphate ion at selected pH values:

| pH | Time (min.) |
|---|---|
| 1 | *c.* 10 |
| 3·5 | 3 |
| 8·0 | 30–40 |
| 11·0 | 300–400 |

The condensed phosphates are well known for their sequestering properties. The presence of the –N(H)– group enhances this effect,[22] so that at pH 12, 100 g. of tetrasodium imidodiphosphate decahydrate sequesters 3·0 g. of calcium (cf. 2·3 for corresponding pyrophosphate).

## NITRIDOTRIPHOSPHORIC ACID AND ITS SALTS



Two acids, containing no amido- or imido-hydrogen, have been described before, namely nitrilodiphosphoric acid (Mellor, VIII, 714,) and nitrilotrimetaphosphoric acid (*ibid.*, 720). Both of their structures were thought to involve four-membered rings, but from general structural considerations this seems unlikely.

The evidence afforded by the preparative technique for the latter compound suggests that this acid may have been nitridotriphosphoric acid, although this is by no means certain.

### Formation and Preparation

If disodium monoamidophosphate is heated *in vacuo* at 210°C., tetrasodium imidodiphosphate is formed, which on further heating at 450°C. loses more ammonia to yield hexasodium nitridotriphosphate[12, 18]:

$$Na_2PO_3NH_2 + H_2NPO_3Na_2 \rightarrow Na_2PO_3N(H)PO_3Na_2 + NH_3$$
$$3Na_2PO_3N(H)PO_3Na_2 \rightarrow 2Na_6(PO_3)_3N + NH_3$$

The free acid has not been isolated.

### Physical Properties

The structure of the nitridotriphosphate ion is thought to be analogous to that of the nitridotrisulphonate, although it is much less stable, and the infra-red spectrum does not exclude the possibility of a linear structure.[129]

Few physical data are available although the infra-red spectrum of the sodium salt has been reported[30] (see Table VIII).

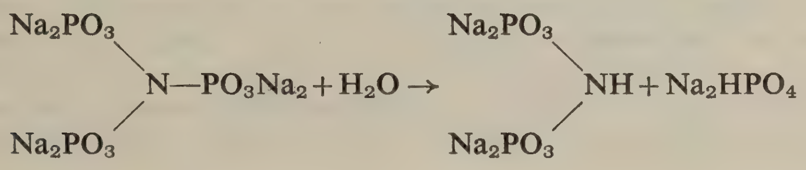
*Table VIII.—Infra-red Spectrum of Hexasodium Nitridotriphosphate*

| Frequency cm.$^{-1}$ | Intensity |
|---|---|
| 1163 | v.s. |
| 1150 | — |
| 1140 | — |
| 1038 | s. |
| 995 | m. |
| 930 | v.s. |
| 740* | s. |
| 617 | w. |
| 580 | v.s. |
| 570 | — |
| 525 | m. |
| 495 | s. |
| 468 | m. |

* Almost certainly antisymmetrical P.N. vibrations.

### Chemical Properties

Hexasodium nitridotriphosphate is very unstable and in the presence of moisture instantly hydrolyzes[12] to yield tetrasodium imidodiphosphate and disodium orthophosphate:

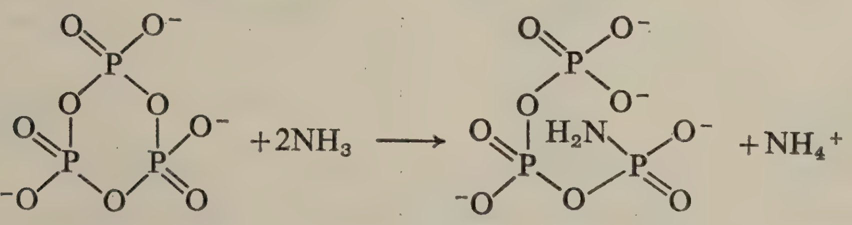


$$(Na_2PO_3)_2N—PO_3Na_2 + H_2O \rightarrow (Na_2PO_3)_2NH + Na_2HPO_4$$

## MONOAMIDOTRIPHOSPHORIC ACID AND ITS SALTS

### Formation and Preparation

Concentrated aqueous ammonia seems capable of severing the trimetaphosphate ring to produce a monoamidotriphosphate. After a solution of trisodium trimetaphosphate and concentrated ammonium hydroxide had been kept at approximately pH 12 for 3 days at 27°C., it was possible to precipitate the barium salt, $Ba_2P_3O_9NH_2$,[48] and other salts by addition of the appropriate cation:



Reaction kinetics were studied using nuclear magnetic resonance techniques. At 26°C., using 0·27 M. trimetaphosphate and 5·8 M. ammonia solution, a first-order reaction constant of $10^{-2}$ min.$^{-1}$ is obtained. In comparison solutions of sodium hydroxide–sodium chloride at the same pH are less effective in bringing about cleavage of the metaphosphate ring.

### Physical Properties

Nuclear magnetic resonance spectra have been obtained from solutions of sodium amidotriphosphate. Measurements were made in an applied field of 9400 gauss at a frequency of 16·2 Mc. The results, expressed in Table IX, give details of the $^{31}P$ multiplets and chemical shifts with respect to 85% orthophosphoric acid.

*Table IX.—Nuclear Magnetic Resonance Spectrum of the Amidotriphosphate Ion*

| Multiplet | Chemical shift (p.p.m. applied field) | Assignment |
|---|---|---|
| Doublet | 0·2 | terminal $PO_4$ |
| Doublet | 5·4 | terminal $PO_3NH_2$ |
| Triplet | 20·7 | central $PO_4$ |

The presence of an amido group displaces the terminal phosphate doublet to a somewhat lower value.

### Chemical Properties

If solutions containing the amidotriphosphate ion are slightly adjusted to pH 3 or 4, the trimetaphosphate ring reforms:

$$2P_3O_9NH_3{}^{3-} \rightarrow P_3O_9{}^{3-} + P_3O_9NH_2{}^{4-} + NH_4{}^{+} \xrightarrow{2H_3O^+} P_3O_9{}^{3-} + NH_4{}^{+} + 2H_2O$$

Evidence of this has been afforded by paper chromatography.[48] The kinetics of this cyclization[105] show that the reaction takes place in two stages. It is acid catalyzed with an average rate constant of $1{\cdot}52 \times 10^{-4}$ min.$^{-1}$ over the pH range 4·5–6·0 (concn. approx. 1 mMol/10 c.c.). Hydrolysis of a 2·3 molar solution of amidotriphosphate with 2 moles of HCl per mole of amidotriphosphate can be shown by paper chromatography to give penta- and hexa-phosphates, presumably by reactions of the type:

$$2P_3O_9NH_2{}^{4-} + 2H^+ + H_2O \rightarrow P_6O_{19}{}^{8-} + 2NH_4{}^{+}$$

Ammonolysis of the amidotriphosphate produces a diamidomonophosphate.

The reaction of trimetaphosphate with primary and secondary amines has also been shown to be reversible, and of first order in both directions, the rate increasing with the dissociation constant of the amine concerned (see Tables X and XI).[135]

*Table X.—Ammonolysis (Aminolysis) of* $[P_3O_9]^{3-}$

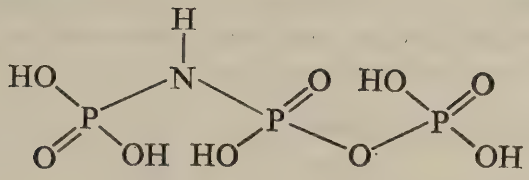
Conc. 0·5 mol $Na_3P_3O_9$ and 0·5 mol $NH_3$ (amine)/l.

| Amine | Dissocn. const. of amine $K \times 10^5$ | Time to reach equilibrium (hr.) | $[P_3O_9NHR]^{4-}$/ original $[P_3O_9]^{3-}$ |
|---|---|---|---|
| $NH_3$ | 1·79 | 20 | 0·48 = 96% |
| $NH_2CH_3$ | 43·8 | 3 | 0·46 = 92% |
| $NH(CH_3)_2$ | 52·0 | 0·5 | 0·40 = 80% |
| $N(CH_3)_3$ | 56·5 | no reaction | |

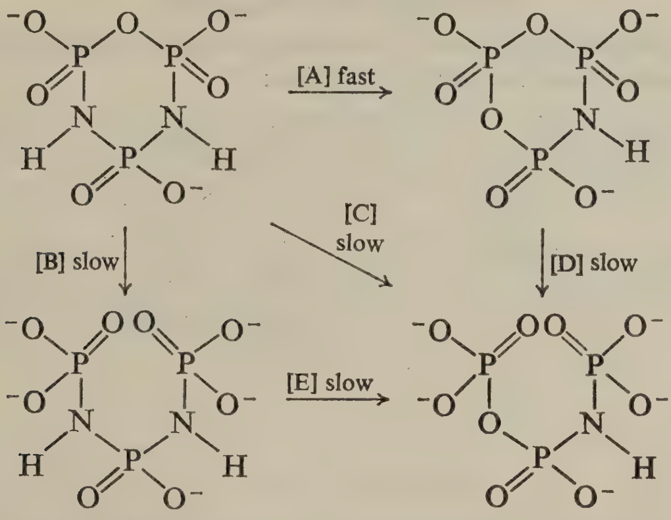
*Table XI.—Recyclization of Amidotriphosphates*
0·1 M. soln., 20°C. pH 6

| Amidotriphosphate | Dissocn. const. of amine $K \times 10^5$ | 1st order velocity const. $k(\text{min.}^{-1}) \times 10^2$ | Half-life (min.) | $k/K$ |
|---|---|---|---|---|
| $[P_3O_9NH_2]^{4-}$ | 1·79 | 1·14 | 60·7 | 637 |
| $[P_3O_9NHCH_3]^{4-}$ | 43·8 | 2·69 | 2·58 | 614 |
| $[P_3O_9N(CH_3)_2]^{4-}$ | 52·0 | 30·2 | 2·30 | 581 |

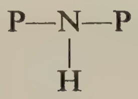
## MONOIMIDOTRIPHOSPHORIC ACID AND ITS SALTS



The imidotriphosphate ion arises as an intermediate in the sequence of reactions resulting from the hydrolysis of trimetaphosphimates, mono- and di-imidotrimetaphosphates or di-imidotriphosphates[46]:

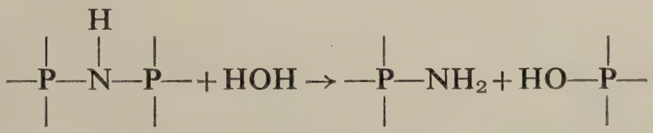


Three distinct reaction mechanisms are involved,[17] namely fission, replacement and condensation;



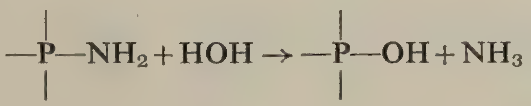
$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{P{-}N{-}P}}$$

bridges are severed hydrolytically:



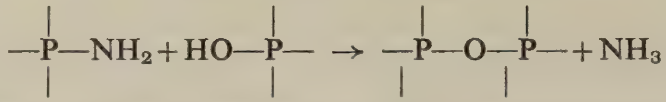
$$-\overset{|}{\underset{|}{P}}-\overset{\mathrm{H}}{\overset{|}{N}}-\overset{|}{\underset{|}{P}}- + \mathrm{HOH} \rightarrow -\overset{|}{\underset{|}{P}}-\mathrm{NH_2} + \mathrm{HO}-\overset{|}{\underset{|}{P}}-$$

and the $-NH_2$ group is replaced by $-OH$:



$$-\overset{|}{\underset{|}{P}}-\mathrm{NH_2} + \mathrm{HOH} \rightarrow -\overset{|}{\underset{|}{P}}-\mathrm{OH} + \mathrm{NH_3}$$

Alternatively deamination occurs with the resultant formation of a P–O–P bridge[49–50]:



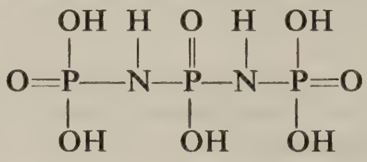
$$-\underset{|}{\overset{|}{P}}-NH_2+HO-\underset{|}{\overset{|}{P}}- \rightarrow -\underset{|}{\overset{|}{P}}-O-\underset{|}{\overset{|}{P}}-+NH_3$$

Naturally this series of reactions does not end at the imidotriphosphate stage, and this ion decomposes into triphosphate, orthophosphate and imidodiphosphate, or monoamidophosphate and pyrophosphate, or very occasionally orthophosphate and amidodiphosphate, which in turn eventually decompose to orthophosphate:

$$P_3O_9NH^{5-}+H_2O \rightarrow P_3O_{10}{}^{5-}+NH_3$$
$$P_3O_9NH^{5-}+2OH^- \rightarrow P_2O_6NH^{4-}+PO_4{}^{3-}+H_2O$$
$$P_3O_9NH^{5-}+OH^- \rightarrow P_2O_7{}^{4-}+PO_3NH_2{}^{2-}$$
$$P_3O_9NH^{5-}+OH^- \rightarrow P_2O_6NH_2{}^{3-}+PO_4{}^{3-}$$

From these reactions it is evident that the decomposition is pH-sensitive, and quarter-lives of the various species have been determined at several pH values. At pH 3·5 imidotriphosphate has a quarter-life of 25 min.[17]

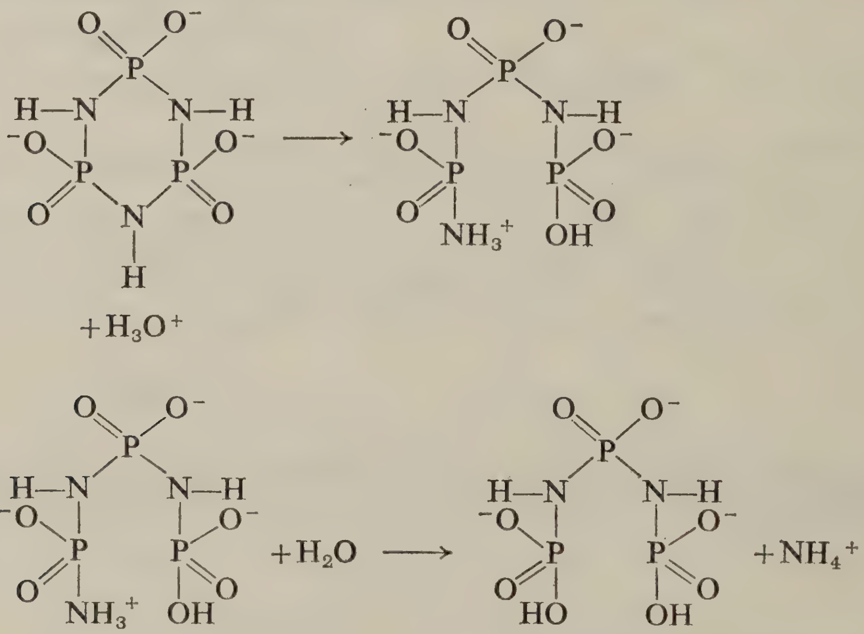
## DI-IMIDOTRIPHOSPHORIC ACID AND ITS SALTS



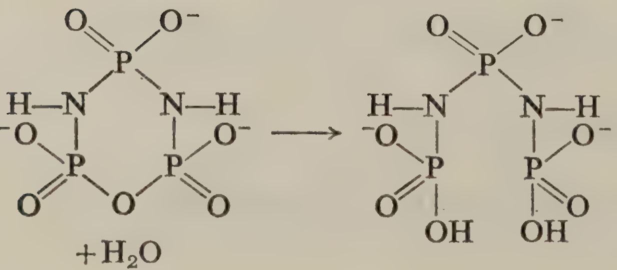
$$O=\underset{OH}{\overset{OH}{P}}-\overset{H}{N}-\underset{OH}{\overset{O}{\overset{\|}{P}}}-\overset{H}{N}-\underset{OH}{\overset{OH}{P}}=O$$

### Formation and Preparation

The di-imidotriphosphate ion arises by the hydrolysis of both trimetaphosphimate and di-imidotrimetaphosphate ions,[17, 45–6] i.e.:



and,

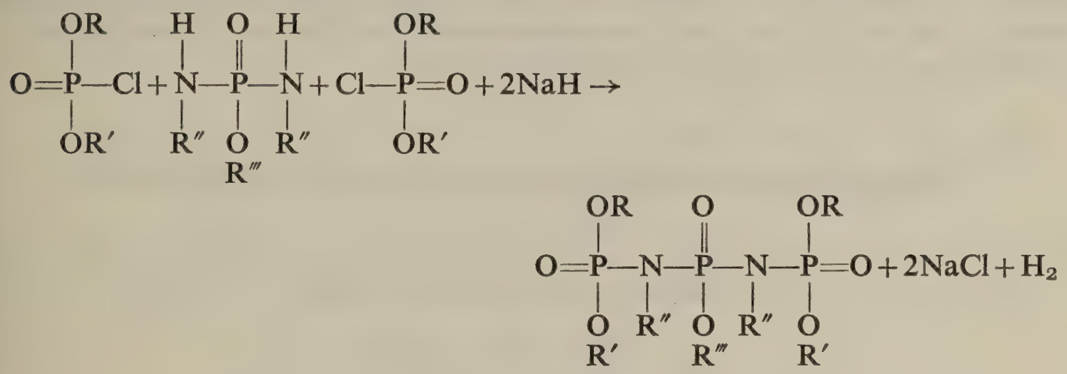


The use of 30% sodium hydroxide solution at 75°C. deposits crystals of sodium di-imidotriphosphate hexahydrate. Because this sort of mechanism operates, various phosphonitrilic derivatives may also give rise to di-imidotriphosphoric acid[51] when hydrolyzed, e.g. trimeric phosphonitrilic diamidotetrachloride:

$$P_3N_3Cl_4(NH_2)_2 + 8H_2O \rightarrow H_5P_3O_8(NH)_2 + 3NH_4Cl + HCl$$

Straight chain materials containing the appropriate skeleton, such as trisodium diamidodi-imidotriphosphate (*q.v.*), can be oxidized in cold aqueous solution by the action of sodium nitrite and perchloric acid.[18] Pentasilver di-imidotriphosphate is precipitated by the addition of silver ions.

It is also possible to produce a di-imidotriphosphate chain by controlled condensation of smaller molecules. Thus it has been claimed that sodium hydride, in the presence of an inert diluent, brings about condensation of diamidophosphates and monochlorophosphates[52]:



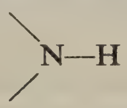
$$O{=}\overset{OR}{\underset{OR'}{P}}{-}Cl + \overset{H}{\underset{R''}{N}}{-}\overset{O}{\underset{OR'''}{P}}{-}\overset{H}{\underset{R''}{N}} + Cl{-}\overset{OR}{\underset{OR'}{P}}{=}O + 2NaH \rightarrow$$

$$O{=}\overset{OR}{\underset{OR'}{P}}{-}\underset{R''}{N}{-}\overset{O}{\underset{OR'''}{P}}{-}\underset{R''}{N}{-}\overset{OR}{\underset{OR'}{P}}{=}O + 2NaCl + H_2$$

### Physical Properties

Trisodium di-imidotriphosphate is very soluble in water, being precipitated by the addition of alcohol as microscopic granules. With slow crystallization the habit is planar, but increases in the rate of crystal growth favour the formation of acicular crystals.

The infra-red spectra of the pentasodium, monosodiumdizinc and pentathallium di-imidotriphosphates show a characteristic absorption region in the range 2900–3200 cm.$^{-1}$ which has been attributed to

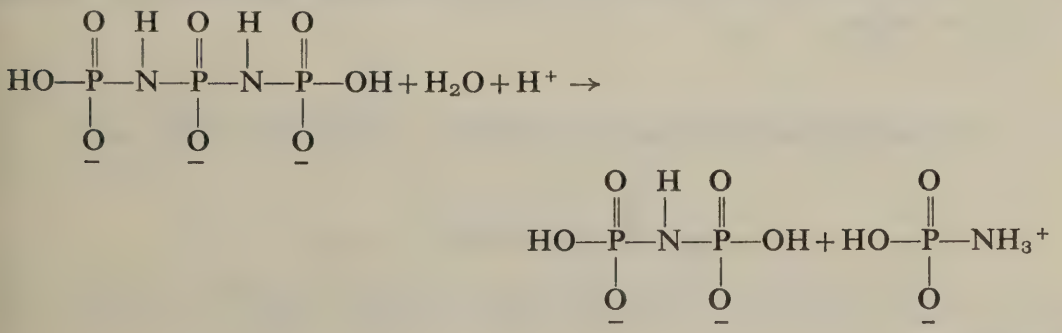


stretching.[21]

### Chemical Properties

Although di-imidotriphosphoric acid is pentabasic, only three inflexions were observed in conductivity[45,53] (see Fig. 7, page 220) and titrimetric[46] curves. The two end points corresponding to pH values 5·0 and 8·6 were very sharp, but that at approximately 10·8 was ill defined.

The appearance of di-imidotriphosphate ion, in the sequence of reactions following the hydrolysis of trimetaphosphimate, provides evidence of its stability. It rapidly decomposes to imidodiphosphate[17,46]:



$$HO{-}\overset{O}{\underset{\underline{O}}{P}}{-}\overset{H}{N}{-}\overset{O}{\underset{\underline{O}}{P}}{-}\overset{H}{N}{-}\overset{O}{\underset{\underline{O}}{P}}{-}OH + H_2O + H^+ \rightarrow$$

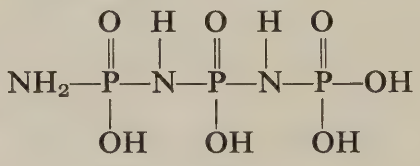
$$HO{-}\overset{O}{\underset{\underline{O}}{P}}{-}\overset{H}{N}{-}\overset{O}{\underset{\underline{O}}{P}}{-}OH + HO{-}\overset{O}{\underset{\underline{O}}{P}}{-}NH_3^+$$

although there is also a rather slower reaction resulting in the formation of imidotriphosphate. To a very limited extent cyclization may also occur. These hydrolyses are pH sensitive and tabulated below is the quarter-life at three selected pH values:

| pH value | quarter-life (min.) |
|---|---|
| 3·5 | 8 |
| 8·0 | 20–30 |
| 11·0 | $(1{\cdot}2\text{–}4) \times 10^3$ |

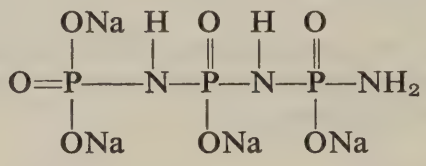
At very high pH values the di-imidotriphosphate ion is very stable and is attacked only slowly by ammonia.[48] Study of the hydrolysis products[106] by the ion exchange technique suggests that the breakdown occurs primarily by protonation of the NH group. The products of hydrolysis have been identified as monoamido, diamido, imidodi, amidodi, ortho- and pyro-phosphates. The last must have formed by condensation between amido and orthophosphates.

## AMIDODI-IMIDOTRIPHOSPHORIC ACID AND ITS SALTS



$$NH_2{-}P(=O)(OH){-}N(H){-}P(=O)(OH){-}N(H){-}P(=O)(OH){-}OH$$

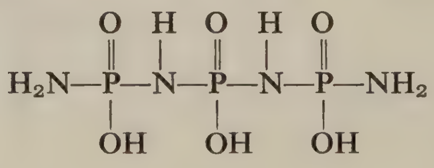
Stoke's observation (Mellor, VIII, 717) of a sodium trimetaphosphimate containing *four* sodium ions per molecule had been regarded as evidence of a linear compound, tetrasodium monoamidodi-imidotriphosphate:



$$O{=}P(ONa)(ONa){-}N(H){-}P(=O)(ONa){-}N(H){-}P(=O)(ONa){-}NH_2$$

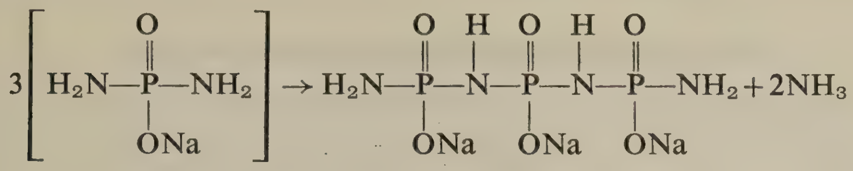
However, the ease with which the free base could be removed by the action of ethanol, and its direct titration, which indicated the presence of one mole of sodium hydroxide per formula weight, suggested the likelihood of an addition compound. By preparing the thallium analogue in the anhydrous state, to avoid masking the infra-red spectra by moisture, it was possible to show that these compounds did not have a linear structure terminating in an amido group. It seems almost certain that the sodium compound has the constitution $Na_3(PO_2NH)_3{,}NaOH{,}8H_2O$, a conclusion supported by the nuclear magnetic resonance spectrum which shows only one type of phosphorus substitution to be present.[21] Later evidence[136] claiming to support the existence of amidodi-imidotriphosphate could be interpreted in terms of the double salt above, but the question could be settled conclusively by an *X*-ray crystal structure determination.

## DIAMIDODI-IMIDOTRIPHOSPHORIC ACID AND ITS SALTS



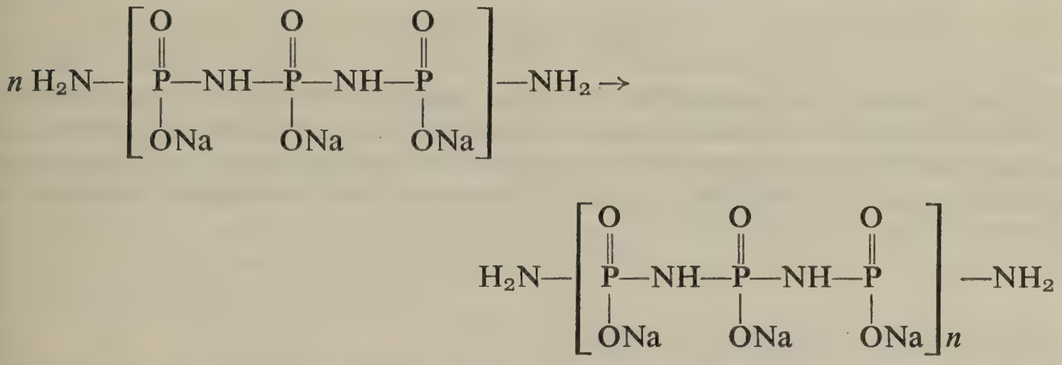
$$H_2N{-}P(=O)(OH){-}N(H){-}P(=O)(OH){-}N(H){-}P(=O)(OH){-}NH_2$$

The free acid is unknown but the trisodium salt is produced[18, 24] by heating monosodium diamidophosphate at 155–165 °C. *in vacuo*:



$$3\left[H_2N-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2\right] \rightarrow H_2N-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-\overset{\overset{H}{|}}{N}-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-\overset{\overset{H}{|}}{N}-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2+2NH_3$$

Prolonged heating causes further condensation to longer chain compounds, e.g.:

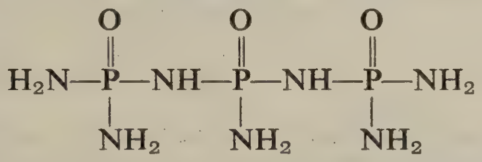


$$n\,H_2N-\left[\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}\right]-NH_2 \rightarrow$$

$$H_2N-\left[\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}\right]_n-NH_2$$

The action of aqueous sodium nitrite and perchloric acid in removing amido groups, provides a convenient method of preparing a di-imidotriphosphate (*q.v.*).

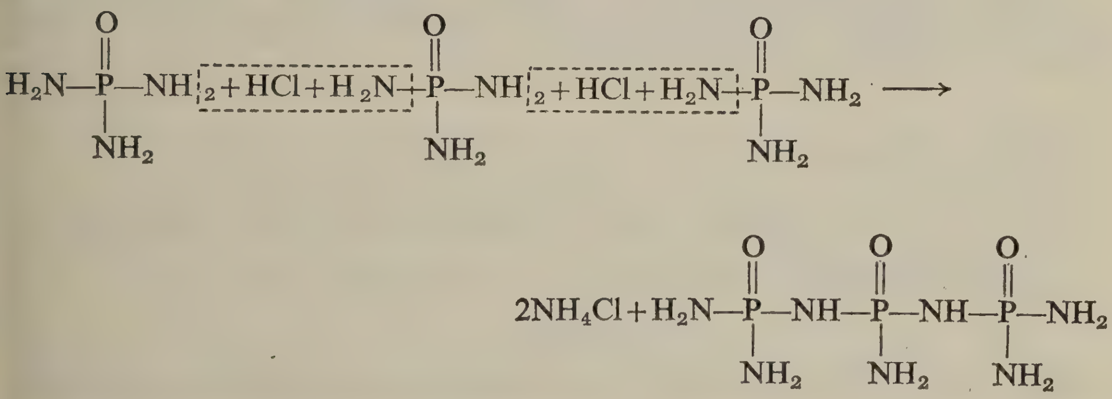
## DI-IMIDOTRIPHOSPHORIC PENTAMIDE



$$H_2N-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2$$

### Preparation

Di-imidotriphosphoric pentamide is conveniently prepared by deamination. A suspension of phosphoryl triamide in diethyl ether is treated with dry hydrogen chloride at 28°–30°C. for 4 hr.



$$H_2N-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH\boxed{{}_2+HCl+H_2N}-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH\boxed{{}_2+HCl+H_2N}-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2 \longrightarrow$$

$$2NH_4Cl+H_2N-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2$$

An 86% yield has been claimed.[35]

To remove traces of ammonium chloride the reaction product is leached with liquid ammonia.

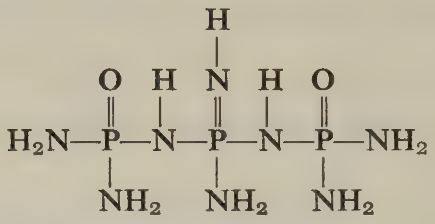
### Properties

Di-imidotriphosphoric pentamide forms white crystals easily soluble in water. When heated the crystals begin to decompose, without melting, at 75°C., losing

**Refs. p. 813**

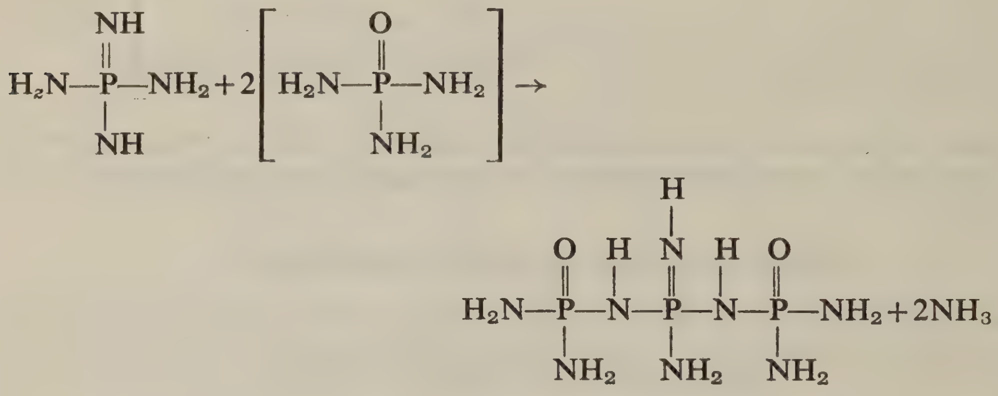
ammonia. The action of sodium hydroxide also brings about the evolution of ammonia, one mole of pentamide yielding 3 moles of ammonia.

## TRI-IMIDOTRIPHOSPHORIC PENTAMIDE



$$H_2N-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-\overset{\overset{H}{|}}{N}-\underset{\underset{NH_2}{|}}{\overset{\overset{\overset{H}{|}}{N}}{\overset{\|}{P}}}-\overset{\overset{H}{|}}{N}-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2$$

Various products are obtainable from the reaction between phosphorus pentachloride and ammonia depending upon the temperature and physical state of the reactants, etc.[33, 54-6] (see page 773). Phosphorimidyl triamide (*q.v.*), which has been suggested as an intermediate, is said to condense with phosphoryl triamide as follows:

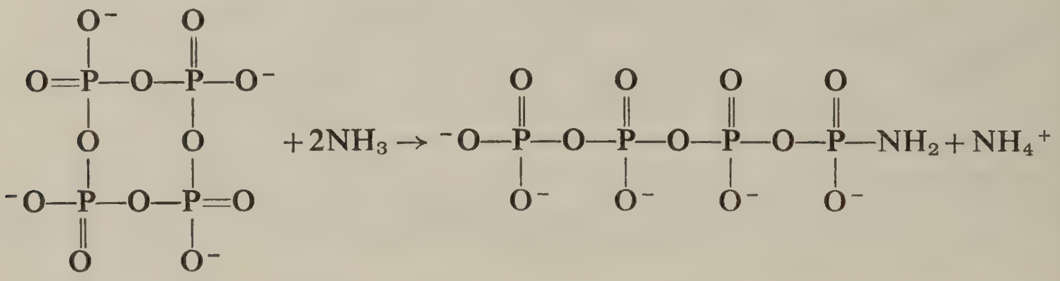


$$H_2N-\underset{\underset{NH}{|}}{\overset{\overset{NH}{\|}}{P}}-NH_2+2\left[H_2N-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2\right]\rightarrow H_2N-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-\overset{\overset{H}{|}}{N}-\underset{\underset{NH_2}{|}}{\overset{\overset{\overset{H}{|}}{N}}{\overset{\|}{P}}}-\overset{\overset{H}{|}}{N}-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2+2NH_3$$

The isolation of tri-imidotriphosphoric pentamide has been reported,[33] the average yield being about 50%. The analysis agreed very well with the calculated composition, but no other information has been published.

## MONOAMIDOTETRAPHOSPHORIC ACID AND ITS SALTS

Concentrated ammonia severs the tetrametaphosphate ring[105] giving rise to amidotetrametaphosphates, the barium salt of which, $[Ba_5(P_4O_{12}NH_2)_2,5H_2O]$, has been isolated. The equation for the reaction is:



Further attack by ammonia results in the production of ammonium triphosphate:

$$P_4O_{12}NH_2^{5-}+2NH_3 \rightarrow P_3O_{10}^{5-}+PO_2(NH_2)_2^{-}+NH_4^{+}$$

## POLYAMIDOPOLYIMIDOPOLYPHOSPHORIC ACIDS AND THEIR SALTS

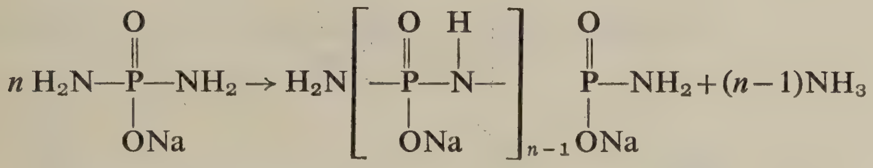
As the chain length of this type of compound increases, the ease with which particular molecules or ions can be separated from each other decreases. Hence, it is convenient to consider under one heading all those acids and salts containing four or more phosphorus atoms, linked in straight or branched chains.

### Formation and Preparation

In general, these compounds are prepared by condensing together smaller molecules containing amido groups, although frequently it is easier to arrange for this condensation, and ammonolysis of halides, oxides, etc., to occur simultaneously. Nevertheless, there are one or two modes of formation which do not fit into this pattern.

One possible method involves the hydrolytic fission of metaphosphimate rings,[58] when chain imidophosphates may be formed momentarily. Another method claims that the treatment of condensed phosphates with ammonia, under high temperature and pressure, gives rise to polyamidopolyimidopolyphosphates.[59] The proportion of amide/imide nitrogen in a given product may be increased by the incorporation of up to 20% by weight of ammonium salts in the reaction mixture, any excess of ammonium salts in the product being removed by leaching with liquid ammonia. Sodium polyphosphates are normally used as starting materials, but potassium and ammonium salts are also suitable.

The most straightforward method of preparing polyamidopolyimidopolyphosphates is to heat the appropriate amidophosphate, preferably *in vacuo* to aid elimination of ammonia. Thus if sodium diamidophosphate is heated *in vacuo* at temperatures between 165° and 200°C., a mixture of diamidopolyimidopolyphosphates is obtained[24]:



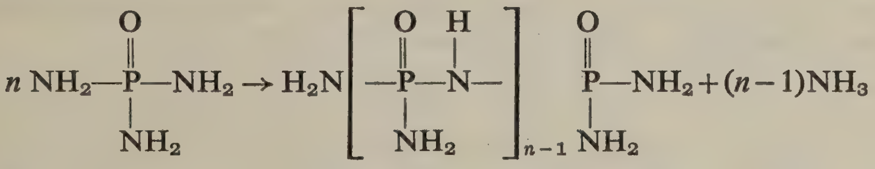
$$n\,H_2N-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-NH_2 \rightarrow H_2N\left[-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-\overset{H}{\overset{|}{N}}-\right]_{n-1}\underset{ONa}{\overset{O}{\overset{\|}{P}}}-NH_2+(n-1)NH_3$$

where $n$ varies between 3 and 6. The degree of condensation seems to depend upon the temperature of reaction, since at a temperature of 230°C. *in vacuo*, chains of approximately 18 phosphate tetrahedra result.[18,24] The molecular weight of these polymeric species has been established in the following way.

The silver salt which is precipitated from an aqueous solution of the sodium compound reacts with ethyl iodide to give a partial yield of the di-ethyl derivative, $NH_2[PO(OEt)N(Et)]_nPO(OEt)NH_2$, in which both imidohydrogen and metal are replaced by ethyl radicals. It is then possible to determine the molecular weight of the ethyl polyethylimidopolyphosphate and hence of the polymeric ion from which it was derived.

By employing an ion exchange resin in the fluoride form[106] the components of the condensation reaction may be separated. Precipitation of the silver salts from the appropriate eluant fraction has led to the isolation of silver diamidoimidodiphosphate, $Ag_2P_2O_4.NH(NH_2)_2$; trisilver diamidoimidodiphosphate, $Ag_2P_2O_4.NAg(NH_2)_2$; silver diamidodi-imidotriphosphate, $Ag_3P_3O_6(NH)_2(NH_2)_2$; pentasilver diamidodi-imidotriphosphate, $Ag_3P_3O_6(NAg)_2(NH_2)_2$, and silver diamidotri-imidotetra-phosphate, $Ag_4P_4O_8(NH)_3(NH_2)_2$.

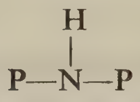
Phosphoryl triamide is readily condensed by boiling its solution in an organic solvent, such as benzene or toluene[19-20]:



$$n\,NH_2-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-NH_2 \rightarrow H_2N\left[-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-\overset{H}{\overset{|}{N}}-\right]_{n-1}\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-NH_2+(n-1)NH_3$$

when polyimidopolyphosphoryl polyamides of chain lengths up to 5 are produced.

This type of reaction is also useful if the diamido-derivative contains an organic radical, since stable non-flammable resins are produced[60-4] containing long



$$\overset{\displaystyle H}{\underset{}{\text{P—}\overset{|}{\text{N}}\text{—P}}}$$

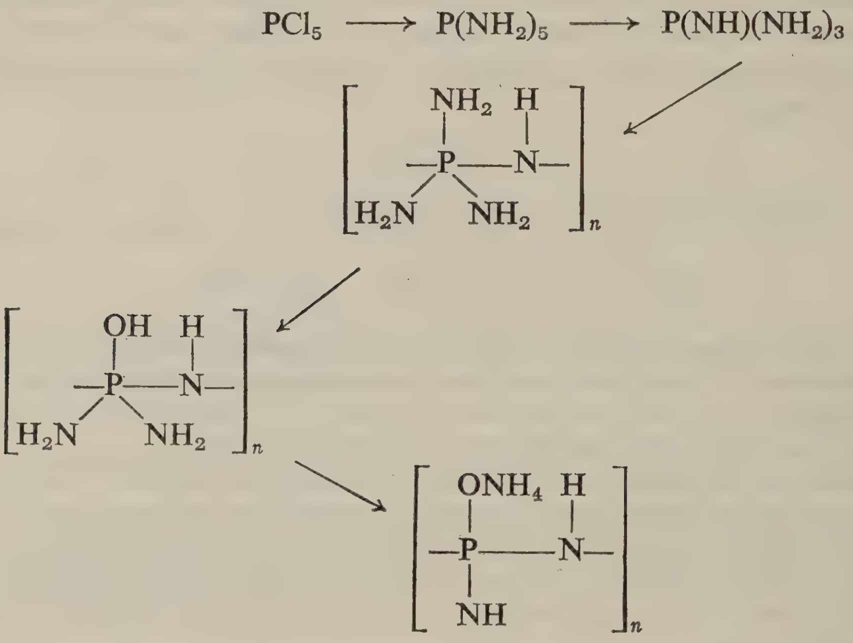
chains. The use of starting materials containing substituted amido groups is also claimed, giving rise to the corresponding substituted imido-polymers.

Often the deamination is encouraged by the presence of a suitable reagent to remove the ammonia. Phosphoryl triamide can be condensed into long chains by treating its suspension in an inert medium with dry hydrogen chloride.[19,34] The chain length seems to depend on the concentration of the hydrogen chloride and the reaction temperature.

Polyamidoimidopolyphosphates do not normally result from the ammonolysis of simple chlorides of phosphorus unless at some stage hydrolysis is allowed to take place.[55] In general polyamides are produced:

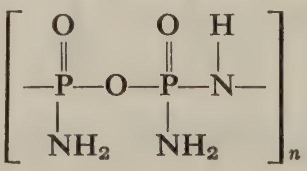
$$PCl_n + 2n\ NH_3 \rightarrow PCl_n{,}2n\ NH_3$$
$$PCl_n{,}2n\ NH_3 \rightarrow P(NH_2)_n + n\ NH_4Cl$$

However, in the presence of a trace of moisture the following reaction sequence has been reported[33]:



Treatment of phosphoryl chloride or its homologues with ammonia has frequently been described.[25,38,43,65-6] In the complete absence of moisture a product of empirical formula $POCl_3{,}6NH_3$ was obtained[55] which could not be rendered free from chlorine by treatment with liquid ammonia. Under similar conditions other workers claimed the formation of a water-insoluble chlorine-free product.[38] If this reaction is carried out in an inert liquid, polymeric products of molecular weights in the range of 180 to 300, and N:P ratios between 2·1 and 2·3 to 1 result. This reaction is general and may be utilized for the preparation of substituted polymers, by using organic amines as alternatives to ammonia.[65]

Provided that the addition of pyrophosphoryl chloride to liquid ammonia is carried out as rapidly as possible, a polymer $(P_2O_3N_3H_5)_x$, i.e.:



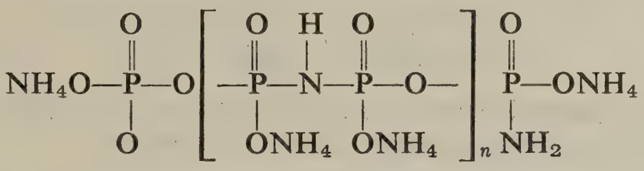
$$\left[ -\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-O-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-\overset{\overset{\displaystyle H}{|}}{N}- \right]_n$$

is obtained,[25, 43, 133] which can be washed free from chloride ion by ice-cold water. Prolonged treatment with ammonia tends to bring about depolymerization to yield very short chain compounds.[25]

The most widely applied methods of preparing polyamidopolyimidopolyphosphates involve the ammonolysis of oxides of phosphorus, frequently prepared *in situ*, under conditions which favour simultaneous deamination. As in the halide ammonolyses (mentioned above) the presence of moisture seems necessary. Although very dry ammonia has been kept for several years over phosphorus pentoxide with no apparent evidence of reaction,[7] it has been reported[9] that even under such dry conditions reaction does take place and is not confined to the solid surfaces.[8]

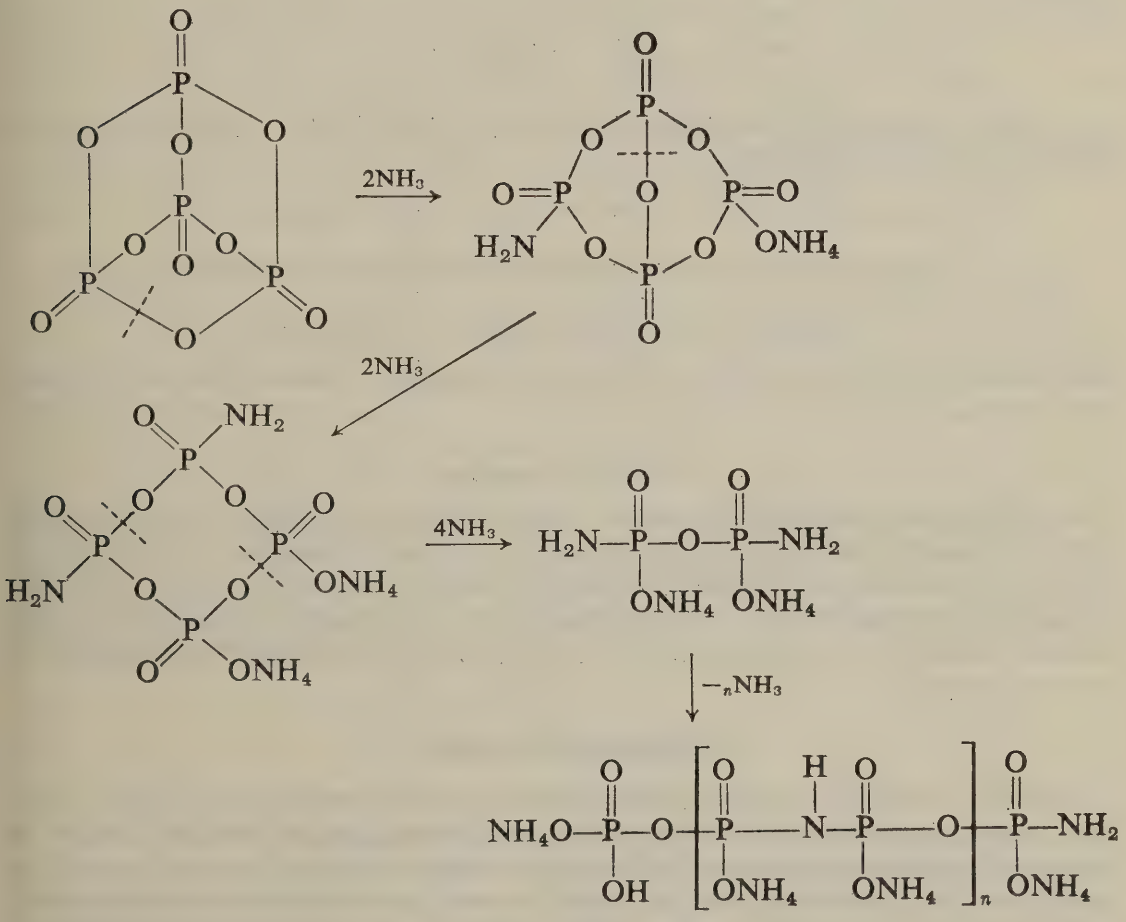
The physical states of the reagents may vary widely. Thus liquid, gaseous, and aqueous ammonia together with solid and gaseous phosphorus pentoxide have been employed.[67, 107] It has also been claimed[68] that ammonium salts such as bicarbonate, acetate or chloride, may be substituted for ammonia, provided the mole ratio $NH_3:P_2O_5$ lies in the range 1·4–2·5:1.

By stirring excess of liquid ammonia with phosphorus oxide in an autoclave for 24 hr. at 40°–50°C., a glassy grey solid is obtained.[10] When this is heated at 100°–110°C. ammonia is evolved, yielding a hygroscopic amorphous grey solid believed to be an ammonium amidopolyimidopolyphosphate, i.e.:



$$NH_4O\text{—}\underset{O}{\underset{|}{\overset{O}{\overset{\|}{P}}}}\text{—}O\left[\text{—}\underset{ONH_4}{\underset{|}{\overset{O}{\overset{\|}{P}}}}\text{—}\overset{H}{\overset{|}{N}}\text{—}\underset{ONH_4}{\underset{|}{\overset{O}{\overset{\|}{P}}}}\text{—}O\text{—}\right]_n\underset{NH_2}{\underset{|}{\overset{O}{\overset{\|}{P}}}}\text{—}ONH_4$$

where *n* is four. The following mechanism has been suggested:



The composition of the ammonium salt is expressed by the ratios:

$$P:N_{total}:N_{ammoniacal} = 1:1{\cdot}5:1$$

In a similar experiment the products fused at 180°–220°C. and a glassy condensed product was formed above 400°C. under pressure from 12 to 50 kg./cm.$^2$; 25% of the nitrogen was not in the ammoniacal form.

In the reaction[107] between phosphorus pentoxide and aqueous ammonia, ammonia losses are counteracted by passing gaseous ammonia into the reaction mixture. The reaction may be carried out by suspending the phosphorus pentoxide in a non-aqueous solvent immiscible with water.[69] In general, mixtures of polyamidopolyimidopolyphosphates are produced which may be obtained as solids by evaporating the solutions under vacuum, by precipitation using non-aqueous solvents, or by spray drying.

Various authorities[70-2, 108] claim that it is advantageous to prepare phosphorus pentoxide *in situ* by burning phosphorus, largely because the gaseous material is then available at a conveniently high temperature. The significant variables for the vapour phase reaction appear to be the $NH_3/H_2O/P_2O_5$ ratio, the temperature of the phosphorus pentoxide vapour and the time interval between mixing the vapours and quenching the product.[67] The preferred ratios are as follows:

| | |
|---|---|
| $NH_3/P_2O_5$ | $0{\cdot}8 \sim 3{\cdot}0$ |
| $H_2O/NH_3$ | $0{\cdot}0 - 2{\cdot}0$ |

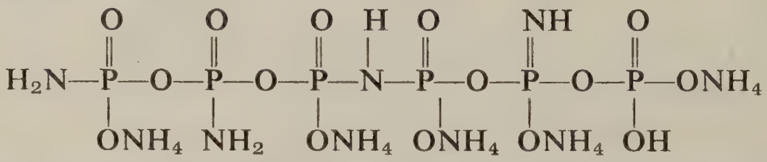
when compounds of general formula $(N'_wH_x)P_nO_yN_z$ result; N′ refers to the ammoniacal nitrogen only. The overall equation may be expressed:

$$(w+z)NH_3 + \frac{n}{2}P_2O_5 + \left(y-\frac{5n}{2}\right)H_2O \rightarrow N'_wH(3w+3z+2y-5n)P_nO_yN_z$$

where

$$y \geqslant \frac{5n}{2}, \qquad \frac{y+z}{n} \geqslant 4$$

A typical compound of empirical composition $9NH_3,3P_2O_5$ may thus have the following possible constitution:



$$H_2N{-}\underset{ONH_4}{\overset{O}{P}}{-}O{-}\underset{NH_2}{\overset{O}{P}}{-}O{-}\underset{ONH_4}{\overset{O}{P}}{-}\overset{H}{N}{-}\underset{ONH_4}{\overset{O}{P}}{-}O{-}\underset{ONH_4}{\overset{NH}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}ONH_4$$

assuming that no rings or P–P bonds and only quadruply linked phosphorus atoms are present.

## Physical Properties

Polyamidopolyimidopolyphosphoric acids and their ammonium and alkali metal salts are usually amorphous greyish-white powders. Although many are very hygroscopic and readily dissolve in water to produce viscous solutions, most of them contain a significant fraction which is insoluble or only slowly soluble in water. The solubility seems to be inversely proportional to the temperature of formation of a given polymer.

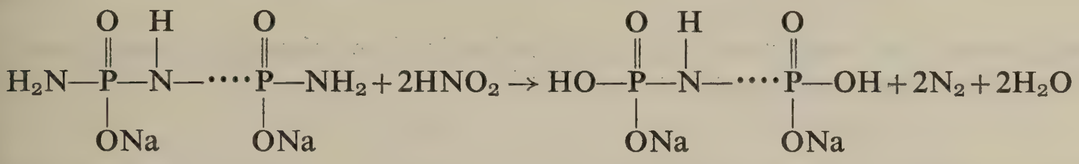
## Chemical Properties

Since the principal preparative technique consists in deaminating smaller molecules, there is a tendency for further elimination of ammonia to take place when the long-chain products themselves are heated *in vacuo* or treated chemically with reagents such as hydrogen chloride. In such a way, polyimidopolyphosphorylpolyamides, $P_nO_n(NH)_{n-1}(NH_2)_{n+2}$, eventually lose all their hydrogen to yield $(PON)_x$.[19]

If, however, these polymers are heated in moist air, they lose all their nitrogen and eventually become polyphosphates,[20] e.g.:

$$Na_nP_nO_{2n}(NH)_{n-1}(NH_2)_2 + n\,H_2O \rightarrow \underset{\text{Graham's salt}}{(NaPO_3)_n} + (n+1)NH_3$$

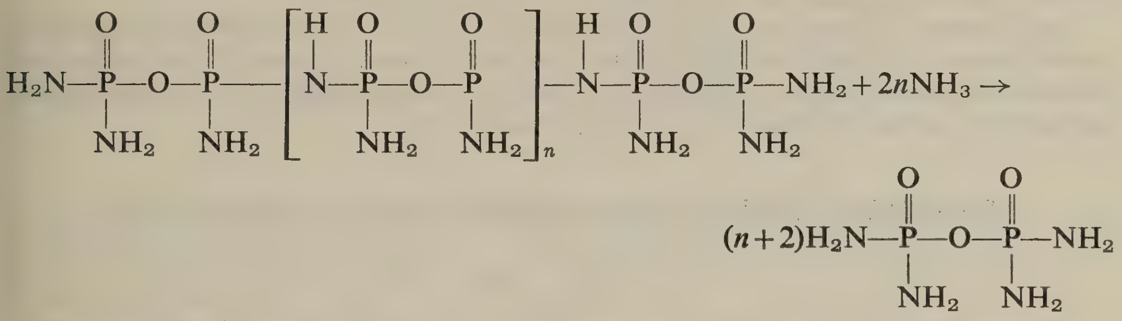
Amido groups, attached to long chains containing phosphorus, oxygen and nitrogen atoms, are selectively removed by treatment with freshly prepared nitrous acid[24]:



$$H_2N-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-\overset{H}{N}-\cdots\underset{ONa}{\overset{O}{\overset{\|}{P}}}-NH_2 + 2HNO_2 \rightarrow HO-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-\overset{H}{N}-\cdots\underset{ONa}{\overset{O}{\overset{\|}{P}}}-OH + 2N_2 + 2H_2O$$

whilst any acid groupings remaining are readily neutralized by treatment with gaseous ammonia[67] in a straightforward acid-base reaction.

To a limited extent deamination is a reversible process, since the solid polymer obtained by rapid addition of ammonia to pyrophosphoryl tetrachloride can be depolymerized by leaching it with liquid ammonia[25]:



$$H_2N-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-O-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-\left[\overset{H}{N}-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-O-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}\right]_n-\overset{H}{N}-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-O-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-NH_2 + 2nNH_3 \rightarrow (n+2)H_2N-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-O-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-NH_2$$

Because of their similarity to polyphosphates, polyamidopolyimidopolyphosphates have found application as additives to rinsing agents and detergents,[59] as water softeners, particularly in the pH range 7–9[68], and as anticorrosion agents.

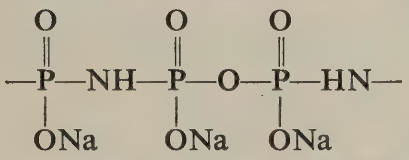
Many of these compounds, particularly the organo-substituted polymers,[60-5] are resins which are suitable for use as flameproofing materials.[37, 109-15]

Several polyamidopolyimidopolyphosphates coagulate albumen[68] and a few have been used as fertilizers,[67, 70-1] although their agronomic value is said to have been improved by hydrolyzing the products to ammonium polyphosphates.[73]

## POLYIMIDOPOLYOXOPHOSPHORIC ACIDS AND THEIR SALTS

If trisodium trimetaphosphimate tetrahydrate is slowly heated to 200°C. in a stream of moist air it decomposes to ammonia, sodium polyphosphates and sodium trimetaphosphate. However, rapid heating yields in addition an insoluble nitrogen-containing residue. This swells in water to a gelatinous mass, which on treatment with ethanol or methanol yields a white amorphous solid.

The N:P molar ratio of this material varies between 0·33:1 and 0·5:1, and with other analytical data suggests formulae between $[(NaPO_3)_2.NaPO_2NH]_n$ and $[(NaPO_3).(NaPO_2NH)]_n$. Similar bodies can be made by thermal condensation at 300°–350°C. of mixtures of sodium dihydrogen phosphate with sodium and ammonium imidodiphosphates. It therefore seems probable that such materials are polymeric sodium imido-oxypolyphosphates containing chains of the type:

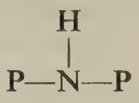


$$-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-NH-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-O-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-HN-$$

In water they slowly hydrolyze to trimetaphosphate, di-imidotrimetaphosphate, and imidotrimetaphosphate, with smaller amounts of mono- and diamidophosphate. When heated in moist air they evolve ammonia, the final product being sodium trimetaphosphate.[137]

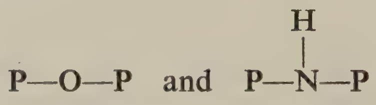
## THE CYCLIC NITROGEN-SUBSTITUTED OXYACIDS OF PHOSPHORUS

This classification is not confined to the metaphosphimic acids since this term usually refers to acids containing



$$P{-}\overset{\displaystyle H}{\overset{|}{N}}{-}P$$

bridges only. It also includes acids such as imidotrimetaphosphoric and di-imidotrimetaphosphoric acids which contain both



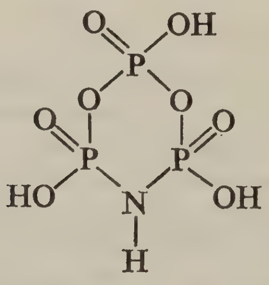
$$P{-}O{-}P \quad \text{and} \quad P{-}\overset{\displaystyle H}{\overset{|}{N}}{-}P$$

bridges.

Previous reports (Mellor, VIII, 716) suggest the possibility of dimetaphosphimic acids, but no evidence for four-membered ring acids has been obtained and the six-membered ring is most likely the first member of each series.

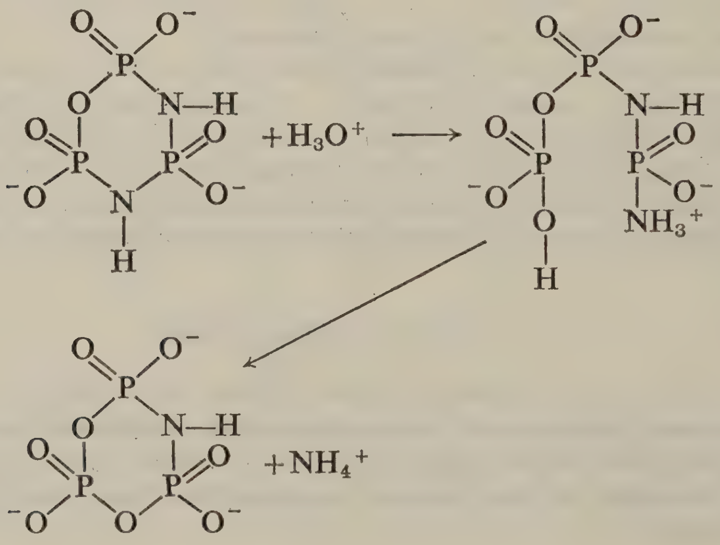
For a general discussion of the properties of cyclic P–N compounds, reference should be made to Section XVIII of this volume. However, most of the compounds considered here do not exhibit many features characteristic of phosphonitrilic derivatives, as they normally contain imido-nitrogen.

## MONOIMIDOTRIMETAPHOSPHORIC ACID AND ITS SALTS

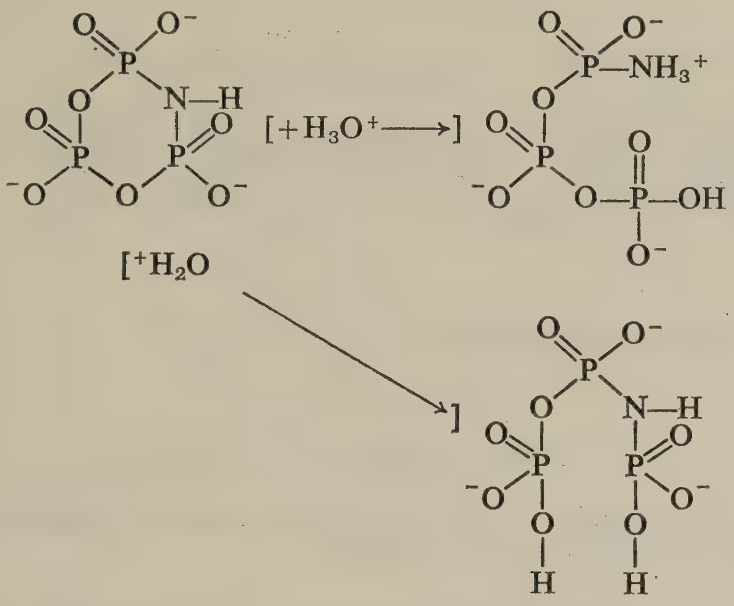


The monoimidotrimetaphosphate ion appears in the sequence of compounds arising from the hydrolysis of trimetaphosphimate.

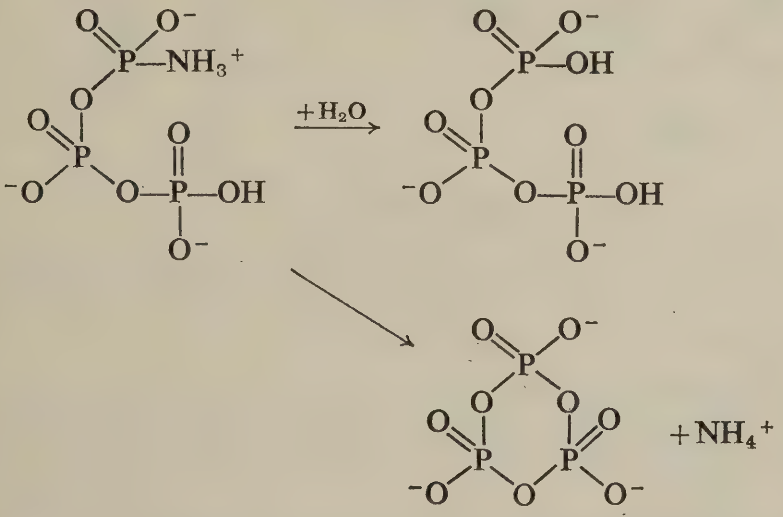
The mechanism is discussed under the chemical properties of trimetaphosphimic acid. Thus, di-imidotrimetaphosphate gives rise to monoimidotrimetaphosphate as indicated below[17,46]:



The process does not cease at this point but continues by stages to yield trimetaphosphate, imidotriphosphate or triphosphate as the pH and the rates of the respective reactions vary. The ring tends to break at one of two possible points depending on the pH, i.e.:

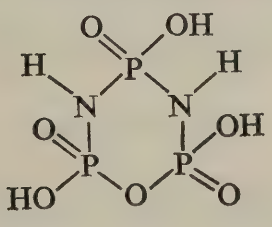


forming either amidotriphosphate or imidotriphosphate respectively. The amidotriphosphate may either decompose to triphosphate or, possibly, recyclize to yield trimetaphosphate[48, 105, 135]:



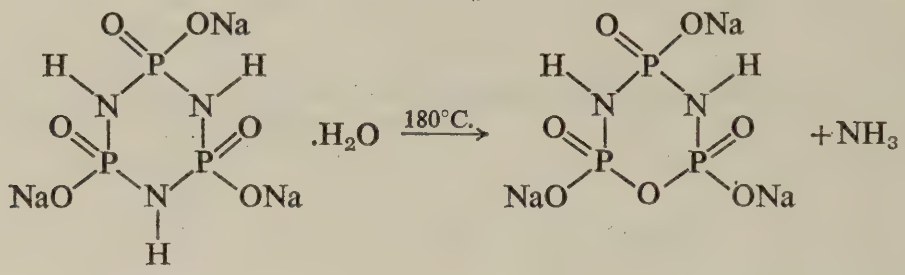
Quarter-life of $1{\cdot}4 \times 10^3$ and 9 to $12 \times 10^3$ min. has been measured[17] at pH 3·5 and 8·0 respectively. It will be noticed that the high pH is associated with a longer quarter-life, which is in harmony with the observation that concentrated aqueous ammonia attacks the imidotrimetaphosphate ring only slowly.[48]

## DI-IMIDOTRIMETAPHOSPHORIC ACID AND ITS SALTS

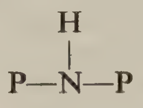


### Formation and Preparation

The formation of sodium di-imidotrimetaphosphate was suggested to account for the loss of ammonia observed when attempts were made to dehydrate sodium trimetaphosphimate monohydrate[74]:

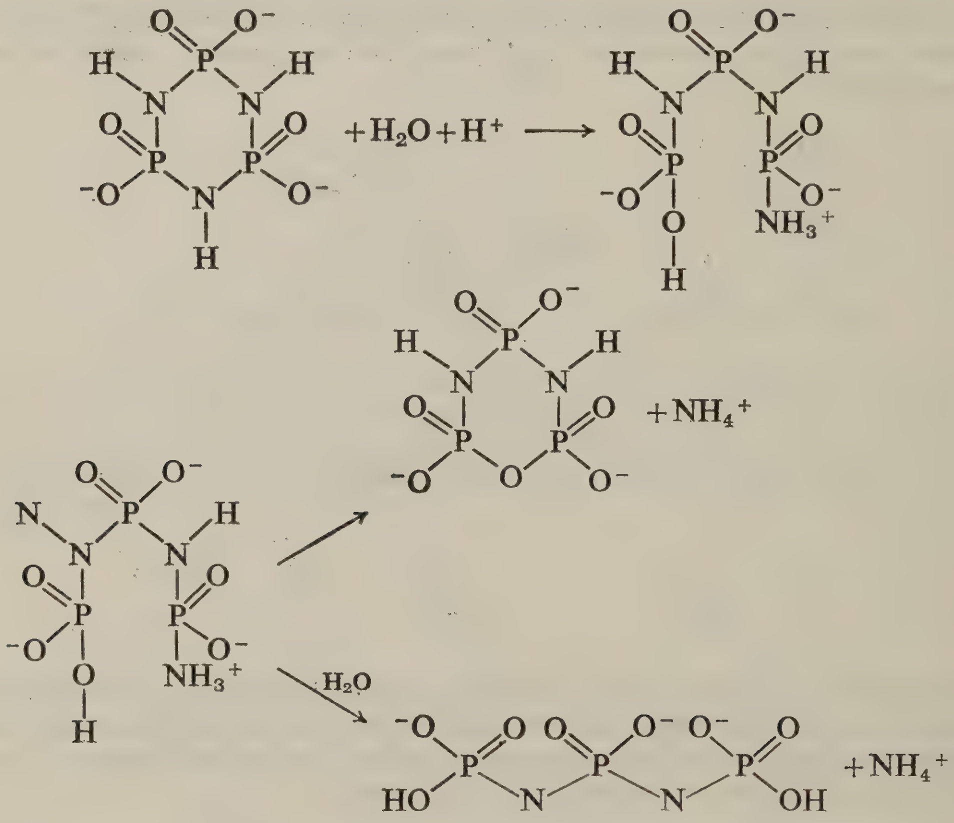


In solution, similar replacement of



$P{-}\overset{\overset{H}{|}}{N}{-}P$ bridges by P—O—P

takes place. The mechanism, which is discussed under the chemical properties of trimetaphosphimic acid, proceeds as follows:



The chain phosphates and imidophosphates are removed, precipitating the silver salt of the metaphosphimic acid and finally exchanging this salt with sodium chloride. The product was identical with that prepared by the method of de Fiquelmont.[45]

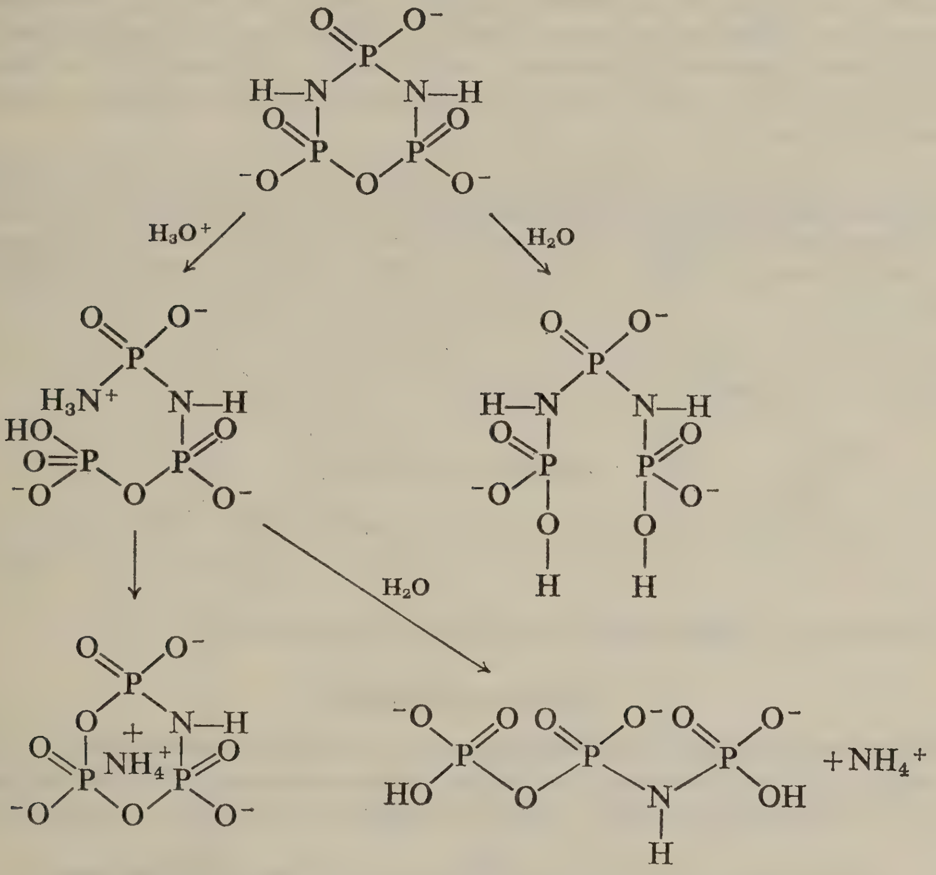
### Physical Properties

*X*-Ray powder diffraction photographs of the sodium salt were not particularly helpful,[74] since the lines were very weak, indicating largely amorphous character.

However, it has been possible to examine the infra-red spectra of the potassium, silver and thallium salts, including an addition compound of thallium di-imidotrimetaphosphate and thallium hydroxide. In all cases there was strong absorption in the 2900–3200 cm.$^{-1}$ region corresponding to >N–H stretching.

### Chemical Properties

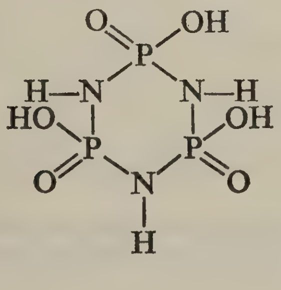
The di-imidotrimetaphosphate ion continues to hydrolyze following the same sort of mechanism by which it was produced, giving rise to imidotrimetaphosphate and to a lesser extent di-imidotriphosphate and imidotriphosphate,[46] as shown below[17]:



The quarter-life is as follows: at pH 3·5, 170 min., and at pH 8·0, 3–9 × $10^4$ min. Consequently at high pH values little hydrolysis may be expected to occur. In fact concentrated aqueous ammonia does not appear to attack the di-imidotrimetaphosphate ion at all.[48]

If sodium di-imidotrimetaphosphate is heated at 270°C. for some considerable time it eventually loses all its nitrogen and becomes anhydrous sodium trimetaphosphate.[74]

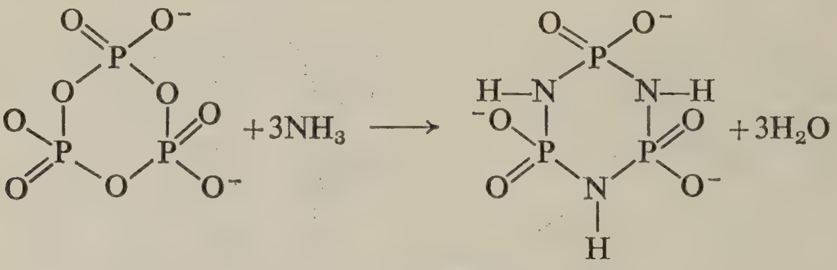
## TRIMETAPHOSPHIMIC ACID AND ITS SALTS



### Formation and Preparation

It is probably most convenient to prepare the trimetaphosphimate ion by hydrolyzing the corresponding phosphonitrilic chloride (Mellor, VIII, 717). Very slight deviations from the original experimental technique[45, 74, 138–9] have proved satisfactory. The hydrolysis of the phosphonitrilic trimer[116] has been studied under neutral conditions and the order in which the chlorine atoms are replaced by hydroxyl groups postulated. However, it is also possible to obtain the trimetaphosphimate ion from higher polymetaphosphimates.[58] Apart from the tetrametaphosphimate, which is rather stable at a pH of 3·6, all the polymetaphosphimates so far investigated appear to decompose, yielding trimetaphosphimate and orthophosphate at the first stage (for a discussion of the probable mechanism see page 810). Anhydrous trimetaphosphimic acid can be obtained from the potassium salt by treatment with perchloric acid, followed by evaporation of the solution at a temperature below 35°C. It forms needle-like crystals, m.p. 150°C. (decomp.). The dihydrate, $H_3[P_3O_6(NH)_3].2H_2O$, m.p. 110°C., is precipitated from aqueous solution by methanolic hexane.[139]

It has been claimed that P–O–P bridges may be replaced by $\mathrm{P{-}\overset{H}{\overset{|}{N}}{-}P}$ bridges by reacting a condensed phosphate with ammonia at elevated temperatures and pressures.[59] Thus the trimetaphosphate ion would yield trimetaphosphimate under these conditions,



but no evidence of this particular reaction has been published.

### Physical Properties

The infra-red spectra of the acid and several salts have been examined[21, 75] including a sample of the anhydrous tripotassium salt containing some deuterated material, i.e. $K_3(PO_2ND)_3$. The principal absorption regions are presented in Table XII.

*Table XII.—The Infra-red Absorption of Trimetaphosphimates*

| Frequency (cm.$^{-1}$) | Assignment |
|---|---|
| 3200–2900* | $>$N–H stretching |
| 1400–1220 | $\mathrm{P{-}\overset{H}{\overset{|}{N}}{-}P}$ group |
| 1300–1200<br>900–850 | $-\mathrm{P}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{O}^{(-)}}$ group |

* $>$N–D stretching occurs in the vicinity of 2390 cm.$^{-1}$

The Raman spectra of trimetaphosphimates have not been studied in detail. However, comparison of the spectra of sodium trimetaphosphimate and the trimetaphosphates of potassium and sodium (see Table XIII), shows that there are differences in frequency of between 50 and 100 cm.$^{-1}$ This has been attributed to the weaker P–N–P bonding compared with P–O–P bonding.[76]

*Table XIII.—Raman Spectra of Trimetaphosphimates and Trimetaphosphates*

| Potassium trimetaphosphate | Sodium trimetaphosphate | Sodium trimetaphosphimate |
|---|---|---|
| 651 | 634 (and 665) | 529 |
| 1111 | 1119 | 1014 |
| 1161 | 1158 | 1109 |
| 1244 | 1243 | 1164 |

The nuclear magnetic resonance spectrum of an aqueous solution of trisodium trimetaphosphimate has been examined in a magnetic field of 7140 gauss.[23] A chemical shift of +1 (±2) p.p.m. of the applied field with respect to 85% phosphoric acid was observed.

An *X*-ray study of trisodium trimetaphosphimate tetrahydrate, $Na_3(NHPO_2)_3$, $4H_2O$, shows that it crystallizes in space group $P2_1/n$ with $Z=4$, $a=16{\cdot}976$; $b=7{\cdot}834$; $c=8{\cdot}918$ A.; $\beta=97{\cdot}08°$. The cyclic anions have a chair shape, and the hydrogen atoms are predominantly linked to nitrogen atoms, as the chemistry would suggest.[140]

## Chemical Properties

Curves obtained by plotting the specific conductivity of the acid against the number of moles of added base (see Fig. 7)

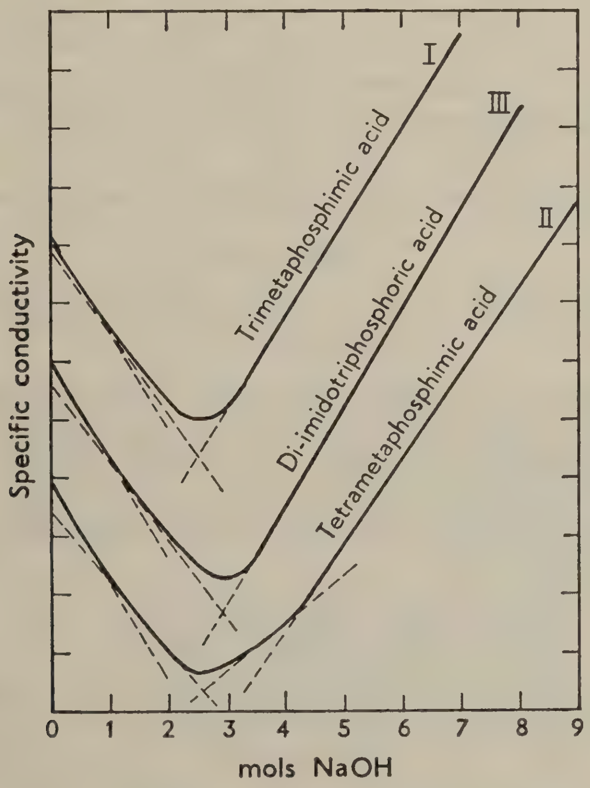


FIG. 7.—Variation in specific conductivity of dilute aqueous solutions of metaphosphimic acids and di-imidotriphosphoric acid during their neutralization with sodium hydroxide

show three inflexions, indicative of three distinct acid functions, the third of which is more feeble than the other two. Doubt is expressed on the identity[53] of the compound hexasilver trimetaphosphimate, $Ag_6P_3N_3O_6$, previously reported by Stokes (Mellor, VIII, 717).

The hydrolytic decomposition of the trimetaphosphimates is pH dependent.[17, 58] The quarter-life has been computed for a series of pH values (see Table XIV).

*Table XIV.—The Quarter-Life of Trimetaphosphate at Various pH Values*

| pH | Quarter-life (min.) |
|---|---|
| 1·0 | 8 |
| 3·5 | 25 |
| 8·0 | $1–2 \times 10^5$ |
| 11·0 | $>2 \times 10^5$ |

The hydrolysis of trimetaphosphimates at 60°C. under mildly acid conditions is considered by Quimby *et al.*[17] to take place as shown on p. 222.

This work was extended by later workers[116-8] using ion exchange and paper chromatographic techniques. Acid hydrolysis of trimeric ring imidophosphates in unbuffered solutions showed a rise in pH with time, Fig. 8, due to the liberation of ammonia and simultaneous formation of other anionic species as shown in the scheme above. These species may be formed by two degradation mechanisms: a complex ring mechanism (I in diagram) or a chain mechanism (II). As it is found that DITMP and ITMP (for abbreviations see diagram, p. 803) appear in the hydrolysis products, the first stage of the hydrolysis might be represented by a complex ring mechanism as follows:

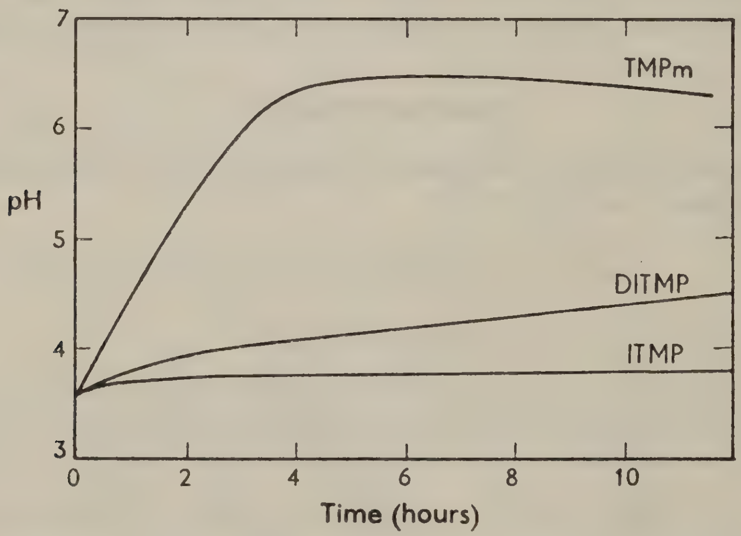
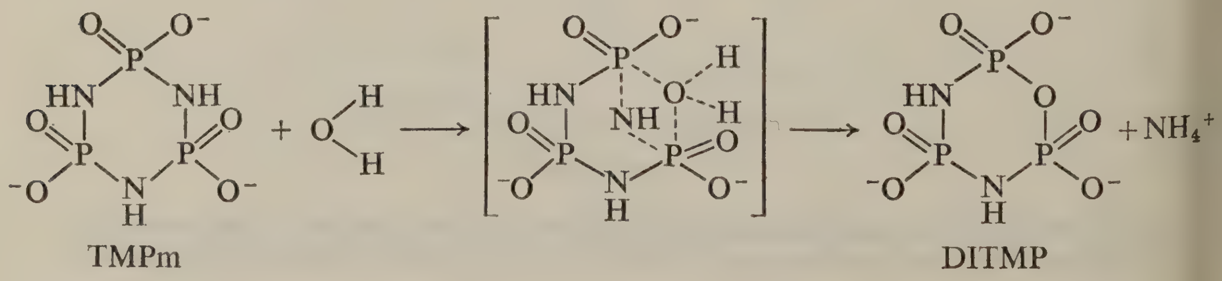
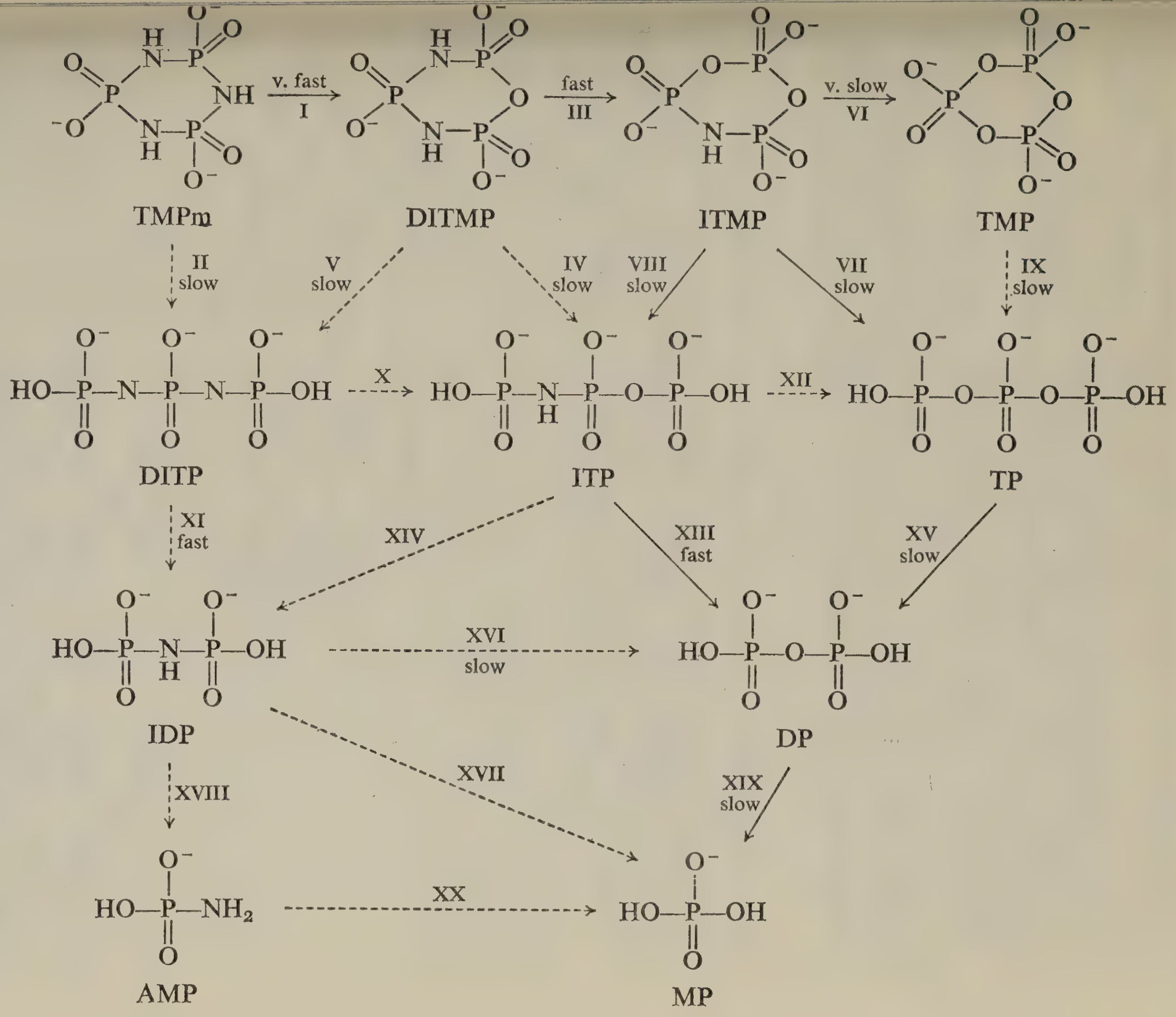


FIG. 8.—Rate of change of pH for the hydrolysis of trimeric ring imidophosphates at pH 3·6 and 60°



| Abbreviation | Name of acid species |
|---|---|
| TMPm | Trimetaphosphimate |
| DITMP | Di-imidotrimetaphosphate |
| ITMP | Imidotrimetaphosphate |
| TMP | Trimetaphosphate |
| DITP | Di-imidotriphosphate |
| ITP | Imidotriphosphate |
| TP | Triphosphate |
| IDP | Imidodiphosphate |
| DP | Pyrophosphate |
| MP | Orthophosphate |
| AMP | Monoamidophosphate |
| ADITP | Amido-di-imidotrimetaphosphate |
| AITP | Amido-imidotriphosphate |
| ATP | Amidotriphosphate |
| TeMPm | Tetrametaphosphimate |

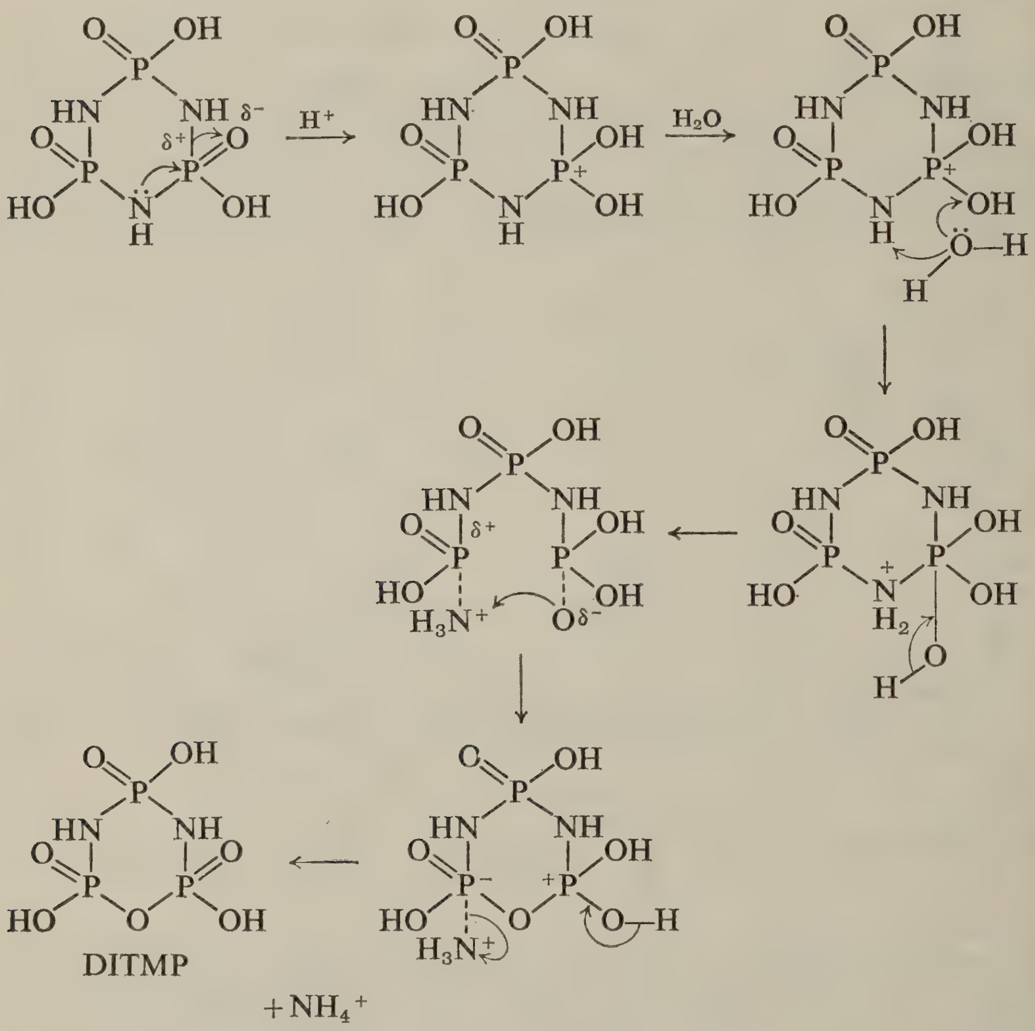


ITMP and TMP should be formed by a similar mechanism. However, as the amounts of TMP formed are very small and orthophosphate appears before TMP is detected, ITMP must hydrolyze by two paths. ITMP can break at the P–O or P–N linkage, the latter giving ITP which easily decomposes to ortho and pyrophosphate.

The argument against the complex ring mechanism is that despite the large size of the 3*d* orbitals of the phosphorus atom these atoms are too far apart for a P–O–P bond to form simultaneously with a P–N–P bond.

The argument against the chain mechanism is that chain imidophosphates are known to break down rapidly in acid solutions. As only DITMP and no orthophosphate is formed immediately and it is considered unlikely that condensation of amidophosphates would occur rapidly, the chain mechanism seems improbable.

A 'ruptured ring' mechanism is suggested incorporating ideas from both alternative mechanisms in which bond rupture and reformation may simultaneously occur.



DITMP

$+NH_4^+$

The steps are thought to occur almost simultaneously. Similar mechanisms are proposed for the hydrolysis of DITMP and ITMP, the rate decreasing in the order TMPm > DITMP > ITMP. An attack at a P–N–P linkage in a ring compound generally gives a ring compound containing a P–O–P link, whilst attack on a P–O–P ring gives polyphosphates.

Two techniques have been employed for measuring the hydrolysis rate:

(*a*) Hydrolysis in buffered solution in which acid was automatically added to maintain the pH at 3·6 permitted the calculation of the approximate hydrolysis rate.

(*b*) Analysis of the hydrolysis degradation products by ion exchange.

The results are presented in Table XV.

*Table XV.—Reaction Constants for the Hydrolysis of Imidophosphates*

| Species | Velocity constant at (min.$^{-1}$) | | Activation energy $E^*$ (kcal./mole) | Differences (kcal./mole) |
|---|---|---|---|---|
| | 60° ref. 117 | 65° ref. 118 | | |
| Trimetaphosphimate | $\sim 8\times 10^{-3}$ | $8{\cdot}91\times 10^{-3}$ | 19·5 | 1·45 |
| Di-imidophosphimate | $\sim 6\times 10^{-3}$ | $1{\cdot}02\times 10^{-3}$ | 20·95 | 1·55 |
| Imidophosphimate | $\sim 7\times 10^{-4}$ | $2{\cdot}30\times 10^{-5}$ | 22·5 | |

The results show that when one imido linkage in a six-membered ring is replaced by an oxygen the ring is stabilized by 1·45 kcal./mole. A further replacement stabilizes the ring by 1·5 kcal./mole. These results are consistent with the value of $E^*$ for sodium trimetaphosphate, 24 kcal./mole, representing a change of 1·5 kcal./mole for the replacement of the last imido linkage in imidotrimetaphosphate.

By heating trisodium trimetaphosphate in moist air at 180°C., it is possible to produce trisodium di-imidotrimetaphosphate.[74] Increasing the temperature to 270°C. results in the appearance of trisodium trimetaphosphate after several hours heating.[74, 141] These reactions do not seem to differ in essence from the hydrolyses discussed immediately above, although it has been suggested that they afford evidence that the degradation proceeds by alternate breaking and reclosure of rings, with loss of ammonia at each stage[141]:

$$\underset{\text{TMPm}}{[P_3O_6(NH)_3]^{3-}} \xrightarrow[-H^+]{+H_2O} \underset{\text{ADITP}}{[H_2NP_3O_7(NH)_2]^{4-}} \xrightarrow[+H^+]{-NH_3}$$

$$\underset{\text{DITMP}}{[P_3O_7(NH)_2]^{3-}} \xrightarrow[-H^+]{+H_2O} \underset{\text{AITP}}{[H_2NP_3O_8(NH)]^{4-}} \xrightarrow[+H^+]{-NH_3}$$

$$\underset{\text{ITMP}}{[P_3O_8(NH)]^{3-}} \xrightarrow[-H^+]{+H_2O} \underset{\text{ATP}}{[P_3O_9.NH_2]^{4-}} \xrightarrow[+H^+]{-NH_3} \underset{\text{TMP}}{[P_3O_9]^{3-}}$$

In view of the dubious existence of some of the intermediates suggested, further evidence for this route is desirable.

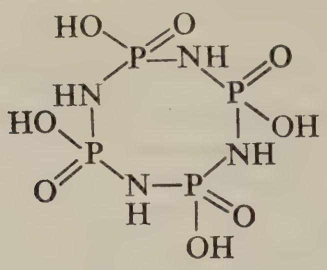
It has been claimed that by the action of various hypochlorites the hydrogen of the imido groups in metaphosphimates can be replaced by chlorine. Provided that the pH lies in the range 4–9 hypochlorous acid is suitable,[77] although metallic hypochlorites may be employed[78] and in certain cases[79] organic hypochlorites, e.g. butyl hypochlorite. The chlorimido derivatives which result are capable of forming addition compounds in much the same way as trimetaphosphimates themselves, e.g.:

$$3[K_3(PO_2NCl)_2.PO_2NH][2KCl][10H_2O]$$

In this particular instance only two imido groups in the ring have been chlorinated, but there appears to be no restriction and a fairly wide range of compounds of general formula $[MPO_2NH_{(n-a)/n}Cl_{a/n}]_n$ may be obtained. A typical example is trisodium trichlorimidotrimetaphosphimate, $Na_3(PO_2NCl)_3,2H_2O$, which crystallizes as parallelogram plates, extinguishing between crossed nicols at 40° to the long sides.

These compounds are readily soluble in water, hydrolyzing under alkaline conditions to release hypochlorite ions which render them suitable for bleaching, disinfecting, oxidizing and chlorinating purposes.

## TETRAMETAPHOSPHIMIC ACID AND ITS SALTS



### Formation and Preparation

The most convenient method[119-20,142] for preparing the tetrametaphosphimate ion is by hydrolyzing the corresponding phosphonitrilic chloride with ammonia or ammonium acetate, the latter giving the purer product. The sodium salt is difficult to isolate as it forms an oil. The simple amido derivatives of the phosphonitrilic chloride tetramer also decompose[45] to give tetrametaphosphimates:

$$P_4N_4Cl_6(NH_2)_2 + 8H_2O \rightarrow P_4N_4O_8H_6(NH_4)_2 + 6HCl$$
$$P_4N_4Cl_4(NH_2)_4 + 8H_2O \rightarrow P_4N_4O_8H_6(NH_4)_2 + 2NH_4Cl + 2HCl$$
$$P_4N_4Cl_6(NH_2)_2 + 10H_2O \rightarrow P_4N_4O_8H_8.2H_2O + 2NH_4Cl + 4HCl$$

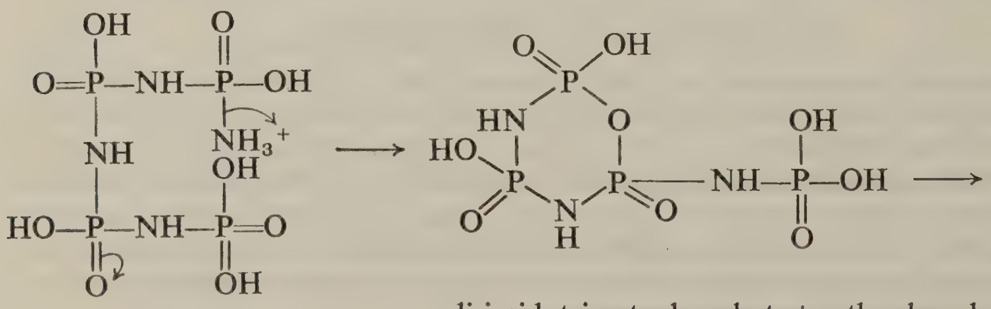
The tetrabasic acid shows an inflexion point at a pK of 3·25. For other properties, except hydrolysis, of this and other polymetaphosphimic acids see page 808.

### Properties

HYDROLYSIS

The hydrolytic decomposition of tetrametaphosphimates is pH-dependent. Only orthophosphates were found when solutions of tetrametaphosphimates were treated with acid at pH 1·0, but at pH 3·6 several species were observed. Ion exchange analyses of the products of hydrolysis of the ammonium salt in a buffer solution of pH 2·0 at 60°C. showed the simultaneous formation of large amounts of orthophosphate and six-membered ring compounds. Allowing for additional orthophosphate formed by hydrolysis, it seemed fairly certain that each tetrametaphosphimate ion formed one orthophosphate and one cyclic ion, probably trimetaphosphimate, which subsequently degraded by way of imidotrimetaphosphate and trimetaphosphate to form orthophosphate.

It is believed that these observations are best explained by a 'ruptured ring' mechanism, the first three major steps of the reaction bring: (1) protonation of a P atom, (2) approach of a water molecule and bonding to a P atom, (3) rupture of the P–N bond taking place as for trimetaphosphimate. The ring formation step would then be:



di-imidotrimetaphosphate + orthophosphate + $NH_4^+$

At pH 3·62 the reaction constant $k_1$ for ring degradation was calculated to be $3{\cdot}37 \times 10^{-4}$ min.$^{-1}$ at 65·0°C. and $1{\cdot}00$–$1{\cdot}01 \times 10^{-3}$ min.$^{-1}$ at 80·0°C. $E^*$ (TeMPm → DITMP) = 17·3 kcal./mole.

## POLYMETAPHOSPHIMIC ACIDS AND THEIR SALTS

The polymetaphosphimic acids, $(H.PO_2NH)_n$, form an homologous series of cyclic compounds of which trimetaphosphimic acid is formally the first member. However, as often happens in such cases, the behaviour of the trimeric acid is somewhat anomalous, and for this reason it has been treated separately here. Tetrametaphosphimic acid is a very stable compound, and to this extent it too is anomalous, although chemically in other respects it resembles the higher members of the series, in so far as they have been investigated. The separation of individual compounds in a pure state becomes progressively more difficult as the series is ascended.

### Formation and Preparation

Polymetaphosphimates are normally prepared by hydrolysis of the appropriate phosphonitrilic derivative (see page 563). The hydrolysis is most conveniently undertaken by dissolving phosphonitrilic chloride in ether and shaking this solution with water[45, 67]:

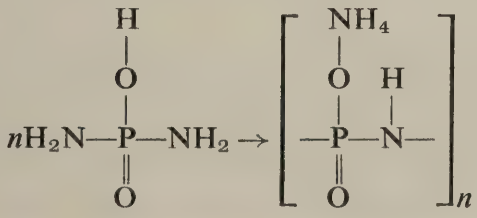
$$(PNCl_2)_n + 2n\ H_2O \rightarrow (PO_2NH)_n^{n-} + 2n\ Cl^- + 3n\ H^+$$

The rate of hydrolysis appears to increase with ring size.

Most alkali-metal salts are readily prepared by straightforward acid-base neutralization procedures, although when the free acid is titrated against standard sodium hydroxide solution the shape of the curve obtained depends to a certain extent on the duration of the experiment.[28] This effect suggests the existence of an equilibrium in which a possible tautomeric form is slowly established.

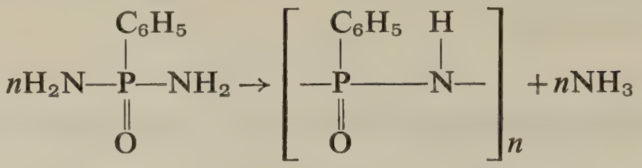
The acid salts can be obtained from the normal compounds by acidifying their solutions (Mellor, VIII, 718). Thus di- and tetra-sodium tetrametaphosphimates, $Na_2H_2(PO_2NH)_4,2H_2O$ and $Na_4(PO_2NH)_4,2H_2O$, have been isolated, although alkali-metal salts are often conveniently prepared by hydrolyzing phosphonitrilic compounds in dilute alkaline media. Diammonium tetrametaphosphimate may be prepared directly from tetrametaphosphimic acid in a rapid reaction with gaseous ammonia; by a much slower reaction the tetrammonium derivative, $(NH_4)_4(PO_2NH)_4$, $4H_2O$, is produced, but the last compound is more effectively prepared in concentrated ammoniacal solution.[45] The preparation of octasilver tetrametaphosphimate (Mellor, VIII, 718) and other silver tetrametaphosphimates containing more than four atoms of silver per molecule is not confirmed.[53]

Claims have been made that the ammonolysis of phosphorus pentoxide, prepared *in situ* from elemental phosphorus, gives rise to a mixture of hygroscopic materials containing between 10 and 30% of ammonium polymetaphosphimate,[71] but there is some doubt as to the nature of this material. However, amorphous hygroscopic ammonium polymetaphosphimate seems to be formed when diamidophosphoric acid is heated to between 100° and 110°C.[10]:



$$n\,H_2N{-}\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{\overset{O}{|}}{P}}{-}NH_2 \rightarrow \left[{-}\underset{\underset{O}{\|}}{\overset{\overset{NH_4}{|}}{\overset{O}{|}}{P}}{-}\overset{\overset{H}{|}}{N}{-}\right]_n$$

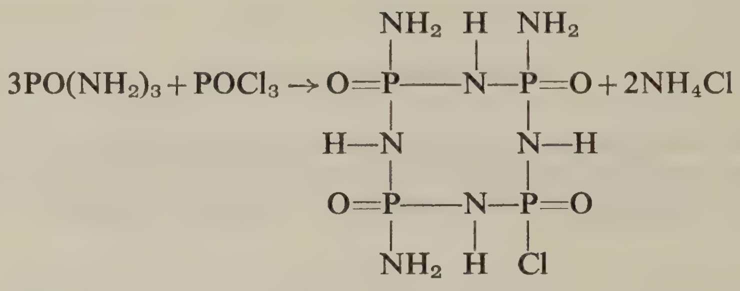
An analogous reaction has been reported[60]:



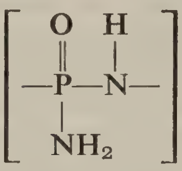
$$nH_2N{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle C_6H_5}{|}}{P}}{-}NH_2 \rightarrow \left[ {-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle C_6H_5}{|}}{P}}{-\!-}\overset{\overset{\displaystyle H}{|}}{N}{-} \right]_n + nNH_3$$

It has been claimed that anhydrous metaphosphates react with ammonia at elevated temperatures and pressures so that a tetrametaphosphate would give rise to the corresponding tetrametaphosphimate.[59] However, bearing in mind the chemical properties of polymetaphosphimates,[58] such a reaction seems improbable.

It is conceivable that an eight-membered ring is formed as a result of the reaction between phosphoryl trichloride and phosphoryl triamide. The following interpretation has been suggested[57]:



When treated with ammonia, the solitary chlorine atom might be replaceable by an amido group to yield fully symmetrical tetrametaphosphimic tetramide, but only a polymer derived from this has been isolated, the structure of which seems uncertain. However, repeating units of the type:



$$\left[ {-}\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}\overset{\overset{\displaystyle H}{|}}{N}{-} \right]$$

are no doubt present.

## Physical Properties

The infra-red spectra of several tetrametaphosphimates have been examined, including the diammonium, the tetrammonium (tetrahydrate), the disodium, the tetrasodium (hydrates), the dipotassium, the tetrapotassium, the tetrasilver, the tetrathallium, the dirubidium, the dicalcium (tetrahydrate), the dibarium (dihydrate), the dicopper (tetrahydrate), the dinickel (2·5 hydrate) and the dilead (hydrate) salts.[21, 75] No common physical properties are given for any of these compounds. The main absorption regions do not differ appreciably from those of the trimetaphosphimates (*q.v.*). The presence of water of crystallization, where it does not mask the absorption, tends to displace much of the absorption to slightly lower frequencies, possibly because of hydrogen bonding to anionic oxygen.

The structure of tetrametaphosphimic acid dihydrate has been studied by *X*-ray diffraction. The compound crystallizes in the orthorhombic system (space group $P2_12_12$) with $a = 13{\cdot}98$; $b = 8{\cdot}32$; $c = 5{\cdot}04$ Å. The evidence, although not firm, indicates that the nitrogen atoms of the ring are linked to hydrogen atoms. There are P–O bonds of two types, differing in length, which are consistent with a formulation of the compound as a hydronium salt, $2H_3O^+.[(NH)_4P_4O_8H_2]^{2-}$.

The anions have the tub configuration with approximate symmetry 4. The P–N bonds are all equal within experimental error, and are longer than is found in phosphonitrilic derivatives, again supporting the 'keto' (metaphosphimic) rather than the 'enol' (phosphonitrilic) structure.[143] Unit cell dimensions for the dihydrate[143] and the dipotassium and dirubidium salts[80] have been recorded (see Table XVI).

*Table XVI.—Orthorhombic Unit Cell Dimensions of Tetrametaphosphimates*

| Compound | *a*(A.) | *b*(A.) | *c*(A.) |
|---|---|---|---|
| Free acid dihydrate | 13·98 | 8·32 | 5·04 |
| Dipotassium salt | 13·89 | 8·07 | 5·03 |
| Dirubidium salt | 14·03 | 8·24 | 5·06 |

This structural analysis of tetrametaphosphimate therefore confirms previous conclusions from infra-red studies[21] that metaphosphimates exist in the $-PO(O^-)-NH-$ form, rather than the tautomeric phosphonitrilic form, $-PO^-(OH)=N-$. For this reason, metaphosphimates would not be expected to exhibit the unique chemical or structural properties of phosphonitrilic compounds, and the term 'phosphonitrilates' is inappropriate to them, but should be reserved for organic derivatives of the type $[(RO)_2P=N]_n$. Potentiometric titrations[121] of the pentametaphosphimate gave two inflexion points corresponding to p$K_1$ values of 2·70 and 6·70. The hexametaphosphimate gave three inflexion points corresponding to p$K_1 = 2·80$, p$K_2 = 6·88$ and p$K_3 = 9·40$.[123]

## Chemical Properties

Metaphosphimic acids behave as polybasic acids, the basicity depending on the number of phosphorus atoms in the ring. Thus tetrametaphosphimic acid has a basicity of four, but conductimetric titrations[53] indicate that the fourth acid function is weaker than the other three (see Fig. 7). In spite of this only two series of salts seem to exist in equilibrium in their aqueous solutions, those in which four hydrogen ions of the acid are replaced by metallic ions, and those in which only two hydrogen ions are replaced. The existence of salts containing eight metallic ions (Mellor, VIII, 718) was not confirmed. A titration curve is shown in Fig. 9, only one inflexion being observed.

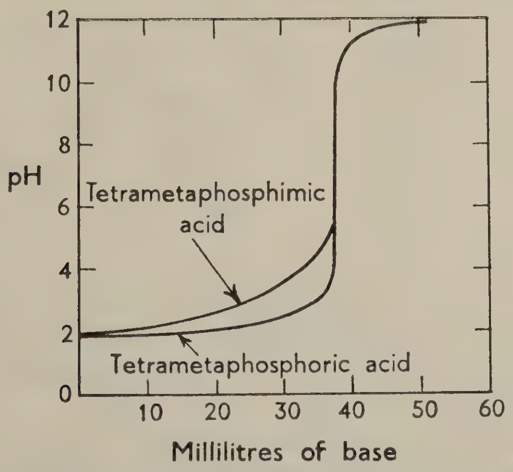


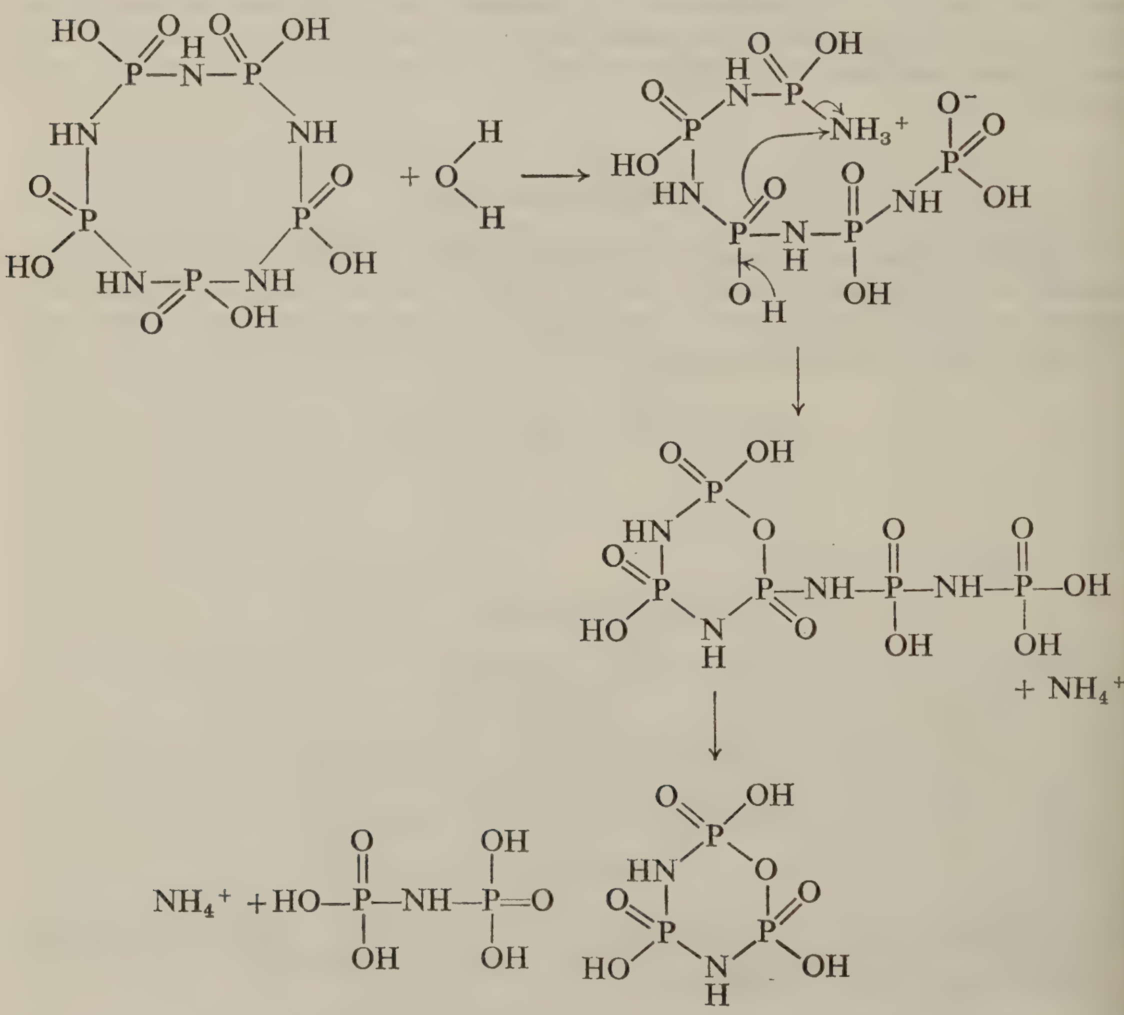
FIG. 9.—Titration curve of tetrametaphosphimic acid compared with that of tetrametaphosphoric acid. The end point of pH equal to about 7 corresponds to one equivalent of base per atomic weight of phosphorus

Polymetaphosphimates are decomposed by the action of heat. Tetrametaphosphimic acid dihydrate was heated under very low pressure (approximately 0·1 mm. mercury) with gradually increasing temperature in the presence of [*sic*] phosphorus pentoxide. At about 100°C. water of hydration was evolved, and in the region of 170°–300°C. a further reaction took place, with loss of ammonia. The product was hygroscopic and gave rise to imidodiphosphoric acid in the presence of moisture, suggesting that a polymeric imidodiphosphoric anhydride had been formed.[44] Above 300°C., further decomposition occurred to phosphorus pentoxide, nitrogen and phosphorus nitride, $(PN)_n$.

Under acidic conditions polymetaphosphimates hydrolyze. By analogy with trimetaphosphimates it would be anticipated that a mechanism involving the successive replacement of P–N(H)–P bridges by P–O–P bridges would operate.

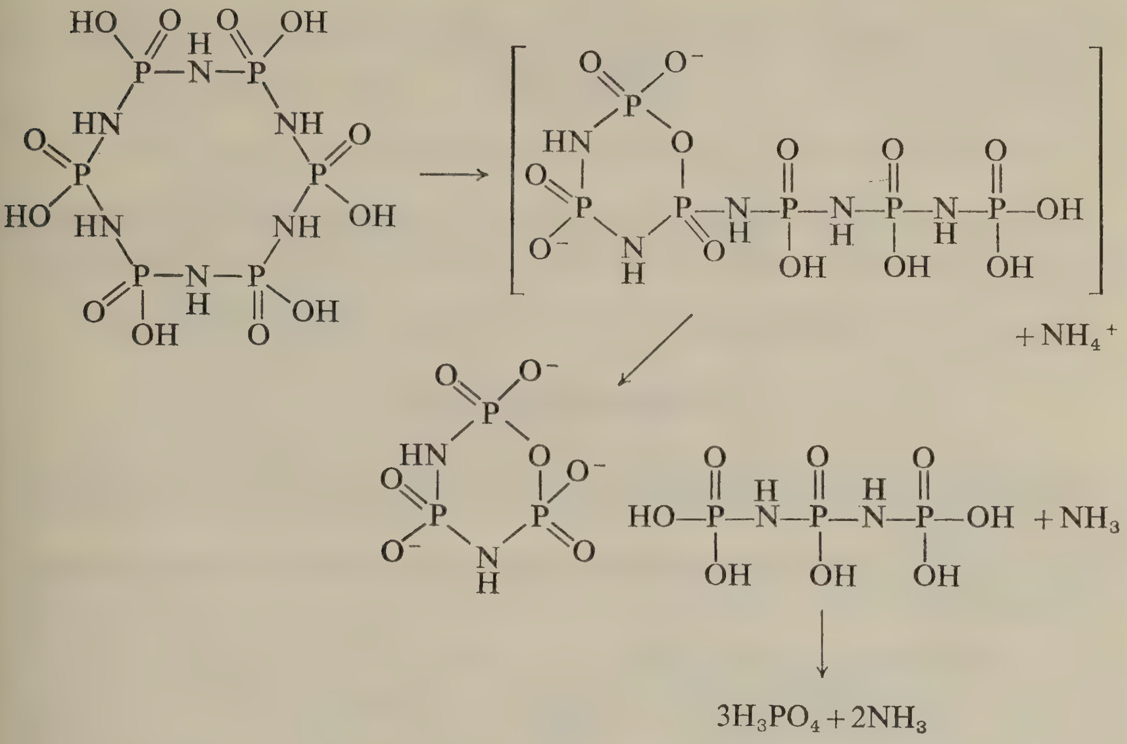
Nevertheless, as with tetrametaphosphimates, similar mechanisms for the hydrolysis of the pentametaphosphimate[121] at pH 3·6 and 60°C. to give trimetaphosphimate and di-imidotrimetaphosphate are thought to occur.

In the 'ruptured ring' mechanism it is again likely that the chain will reform into a six-membered ring, forming a polyimidotrimetaphosphate and eliminating imidodiphosphate. Under the reaction conditions the latter immediately hydrolyzes to ortho- and pyrophosphates:

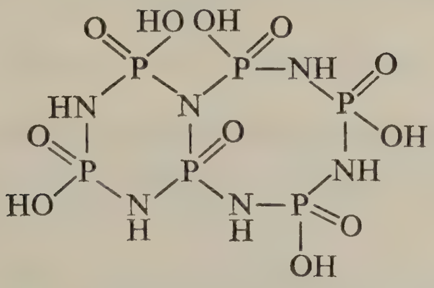


The small amounts of trimetaphosphimate which are also formed may be accounted for by bonding taking place between a nitrogen and a phosphorus atom on opposite sides of the ring. Examination of models shows that in pentametaphosphimate these atoms could indeed be in close proximity.

The hydrolysis of the hexametaphosphate[123] is thought to occur by two mechanisms, one giving di-imidotrimetaphosphate and orthophosphate by a 'ruptured ring' mechanism:



and the other giving trimetaphosphimate or tetrametaphosphimate and orthophosphate by intra-annular cyclization, e.g.:



There is no evidence that this process can take place more than once.

Quantitative hydrolysis of the heptametaphosphimate[122] suggests that the first step is the formation of a trimeric imidophosphate, together with small amounts of trimetaphosphimate which is probably formed by a mechanism like that already discussed.

There appears to be some conflict between the mechanism envisaged above and the claim[73] that ammonium polymetaphosphimate can be hydrolyzed to ammonium polymetaphosphate, which is resolved only if the latter salt is in fact the trimetaphosphate.

Polymetaphosphorochlorimidates may be prepared by treating metaphosphimates with hypochlorites, either as hypochlorous acid,[77] or metallic[78] or organic hypochlorites.[79] Derivatives of tetrapotassium and tetrasodium tetrametaphosphimates have been reported, as in Table XVII.

Polymetaphosphimates exhibit properties typical of polyanions of high molecular weight; for instance egg albumen is immediately coagulated by a polymetaphosphimate solution.[10]

*Table XVII.—Some Tetrametaphosphorochlorimidates*

| Formula of compound | Crystal habit | Optical extinction |
|---|---|---|
| $Na_4(PO_2NCl)_4.9H_2O$ | parallelogram plates | parallel long side |
| $Na_4(PO_2NCl)_4.14H_2O$ | parallelogram plates | 72° to long side |
| $Na_4(PO_2NCl)_4.25H_2O$ | acicular prisms | parallel long side |
| $K_4(PO_2NCl)_4.6H_2O$ | rhomboidal plates | with diagonals |

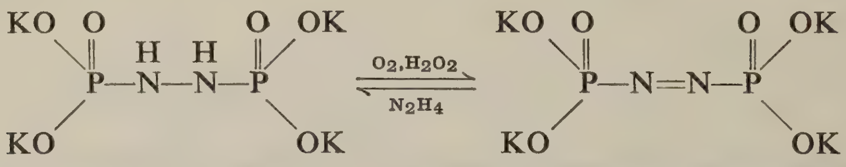
Like linear and cyclic condensed phosphates, solutions of polymetaphosphimates such as the ammonium salts have a slightly alkaline pH and show sequestering properties.

Mixtures of polymetaphosphimates have found application as fertilizers.[71]

## AZO-DIPHOSPHONATES

Alkaline hydrolysis[124] of the tetraphenyl ester of hydrazine diphosphonic acid with potassium hydroxide under nitrogen results in the formation of the tetrapotassium salt, $K_4N_2H_2P_2O_6$.

This salt can be oxidized by hydrogen peroxide or oxygen according to the following equation:



The salt of azo-diphosphonic acid thus formed is bright red in colour and decomposes at a temperature above 300°C. before reaching its melting point. The decomposition may be represented by the following equation:

$$K_2O_3P—N{=}N—PO_3K_2 \xrightarrow{300°} N_2 + K_2O_3P—PO_3K_2$$

Hydrolytic breakdown of the compound produces nitrogen and hydrazine:

$$2K_2O_3P—N{=}N—PO_3K_2 + 4H_2O \xrightarrow{[H^+]} N_2 + N_2H_4 + 4K_2HPO_4$$

## THE ANALYSIS OF NITROGEN-SUBSTITUTED OXYACIDS OF PHOSPHORUS

The value of classical methods of chemical analysis to investigate the chemistry of the nitrogen substituted oxyacids of phosphorus was amply demonstrated by Stokes (Mellor, VIII, 705 *et seq.*). Nevertheless, such methods have severe limitations, particularly when the compounds have similar chemical properties and structures, and more modern physical methods have been employed to good advantage.

*X*-Ray powder diffraction patterns have been examined by a large number of investigators and several details have been published.[12,18,22,29,31,33,35,39,42,45,57] To a limited extent nuclear magnetic resonance spectroscopy is a useful diagnostic tool.[22-3,48]

It is, however, the application of paper chromatography which has been of the greatest value in this field. The majority of recent investigators have employed this technique.[10,12,17,20,22,25 46,58,86] A solvent system which has proved particularly satisfactory[47] is prepared from *iso*propanol (20 parts), dimethylformamide (20 parts), methyl ethyl ketone (20 parts), 25% ammonia solution (1 part) and water (39 parts).

**Refs. p. 813**

From the $R_f$ values (see Table XVIII) the chain lengths ($n$) were estimated from an equation of the form:

$$\ln P_k = -an+b$$

*Table XVIII.—Paper Chromatography of Nitrogen-Substituted Oxyacids of Phosphorus*

| Ion | $R_f$ value | $P_k$ |
|---|---|---|
| orthophosphate | 0·40 | — |
| amidophosphate | 0·44 | — |
| diamidophosphate | 0·57 | 100 |
| phosphoryl triamide | 0·58 | — |
| pyrophosphate | 0·29 | — |
| imidodiphosphate | 0·32 | — |
| diamidoimidodiphosphate | 0·46 | 79·5 |
| diamido-imidotriphosphate | 0·37 | 63·7 |
| diamidotri-imidotetraphosphate | 0·30 | 50·9 |
| diamidotetrimidopentaphosphate | 0·24 | 39·7 |
| diamidopentimidohexaphosphate | 0·18 | 30·9 |
| trimetaphosphimate | 0·43 | — |

Thin layer chromatography, like paper chromatography, has been applied to the analysis of mixtures of phosphorus oxyacids, and a critical comparison of the two methods has been published.[144]

Ion exchange chromatography[58] has been applied successfully to determine the nature of the hydrolysis products of polymetaphosphimates. This technique involves eluting the resin with progressively increasing concentrations of electrolyte so that the ions are desorbed successively.

A microchemical procedure has been developed[81] in which *o*-tolidine, ammonium or silver salts of the appropriate acid are prepared and examined under the microscope. The results are compared with standard micrographs in order to identify the compounds, as opposed to separating them.

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## SECTION XXIX

# PEROXOPHOSPHORIC ACIDS AND THE PEROXOPHOSPHATES

BY J. E. SUCH

## PEROXOPHOSPHORIC ACIDS

### Preparation

ALTHOUGH hydrogen peroxide solutions have not been observed to react with orthophosphoric acid, they do so with pyrophosphoric acid and higher linear polyphosphoric acids[31] to form the so-called peroxomonophosphoric acid, $H_3PO_5$, and other peroxopolyphosphoric acids, such as $H_4P_2O_8$, according to equations of the type[1]:

$$\text{(i)} \qquad H_4P_2O_7 + H_2O_2 = H_3PO_5 + H_3PO_4$$

$$\text{(ii)} \qquad H_4P_2O_7 + H_2O_2 = H_4P_2O_8 + H_2O$$

In aqueous solution, peroxomono- and peroxodi-phosphoric acids are said to exist in equilibrium according to equation (iii):

$$\text{(iii)} \qquad H_4P_2O_8 + H_2O \rightleftharpoons H_3PO_5 + H_3PO_4$$

the formation of products on the right-hand side being favoured by acid and on the left by alkaline conditions.[2-3]

The reaction between the volatile hexagonal (H) form of phosphoric oxide and solutions of hydrogen peroxide, of 30% by weight concentration and above, is extremely violent and can only be carried out successfully by slow addition of small portions of the oxide to well-cooled and vigorously stirred hydrogen peroxide solutions.[1]

However, the vigour of this reaction may be moderated in two ways:

(*a*) If the reactive (H) form of the anhydride is suspended in an inert organic solvent, such as acetonitrile,[4] hydrocarbons, fluorocarbons,[32] or even in orthophosphoric acid itself,[5] hydrogen peroxide of high concentration can then be introduced into the well-cooled and stirred system without excessive loss of active oxygen by decomposition either of hydrogen peroxide or of the peroxoacid itself.

In a typical experiment, using acetonitrile, the following procedure is described: 5·18 millimols. of phosphoric oxide is suspended in 1 mol. of acetonitrile and cooled in a freezing mixture. A solution of 12·34 millimols. of hydrogen peroxide and 3·84 millimols. of water in 1·05 ml. of acetonitrile is added slowly to the well-stirred cooled suspension of phosphoric oxide. Some escape of gas occurs, accompanied first by the odour of ozone and then by the characteristic peroxoacid odour associated with peroxomonosulphuric and peroxo-benzoic acids. After being kept for 24 hr. at room temperature, the solution contains 57% of the added active oxygen in the form of $H_3PO_5$ and 18·5% as hydrogen peroxide. It is believed that most of the peroxoacid formation and the loss of peroxide occur during the first hour of the reaction. After addition of dibenzyl sulphide to the acetonitrile solution, to remove active oxygen as dibenzyl sulphoxide, the residual acid shows equal titrations with alkali, up to the methyl orange indicator change point, and from this stage to the phenolphthalein indicator colour change. Although this property equally well indicates that the acid formed is either orthophosphoric or pyrophosphoric acid, it has been claimed[4] that the chemical properties of the original solution support the view that the main product of the initial reaction is $H_3PO_5$. When ether or *iso*amyl alcohol is substituted for acetonitrile as the inert organic solvent, the reaction between hydrogen peroxide and phosphoric oxide is not so complete, the product containing only 9% or 17% respectively of the added active oxygen as $H_3PO_5$.

Preparations using orthophosphoric acid as the suspension medium are claimed to give products containing much higher proportions of peroxomonophosphoric acid than those previously mentioned, but at the same time some peroxodiphosphoric acid is formed.[5] For example, the best yields are obtained when phosphoric oxide, hydrogen peroxide and water are in the mole ratio of 1 : 2 : 1, and provided good mixing and cooling are applied, high strength (85–95%) hydrogen peroxide can be safely used. If the reaction temperature is kept below 35°C., a typical product contains 71·2% of the added active oxygen in the form of $H_3PO_5$, 1·4% in the form of $H_4P_2O_8$ and 21·4% as $H_2O_2$. The excess of hydrogen peroxide may be removed from the solution by distillation *in vacuo*, at temperatures preferably below 50°C., to give substantially pure peroxomonophosphoric acid.

(*b*) The volatile (H) form of phosphoric oxide can be converted into one of the more complex and less reactive forms by heating it, for example, for 16 hr. at 500°C. under a reduced pressure of 10 mm. Hg. In contrast to the (H) form, the heated oxide reacts only very slowly with high-strength hydrogen peroxide (50–90% $H_2O_2$), complete solution requiring up to 20 hr. or more.[6] The proportion of peroxoacids formed is, however, much less than that obtained by the methods described under (*a*).

Phosphoric oxide did not react with anhydrous (100%) hydrogen peroxide in dry liquid ammonia, even at room temperature under pressure, and the products of reaction in chloroform suspension could not be separated. The reactants combine vigorously if mixed without a diluent, giving permonophosphoric acid and the lower polyphosphoric acids.[37]

The mechanism of the step-wise interaction between hydrogen peroxide and the various forms of phosphoric oxide has not yet been investigated as thoroughly as the aqueous hydration process.

Peroxodiphosphoric acid is obtained, together with pyrophosphoric acid, by the hydration of tetraphosphorus hendecaoxide (*q.v.*)[38]

$$P_4O_{11} + 4H_2O \rightarrow H_4P_2O_8 + H_4P_2O_7$$

Attempts have been made to separate pure permonophosphoric acid from orthophosphoric acid, using ion exchange resins. The separation was successfully achieved in acetonitrile solution (cf. [4]) on a Deacidite FF strong base resin column in its acetate form, by elution with an acetate buffer at pH 5. Concentration of the eluate *in vacuo*, and removal of metal ions by a cation exchange resin in its $H^+$ form, gave a solution containing acetic acid and 95% of the original peroxo-oxygen. Removal of the acetic acid and further concentration by vacuum distillation and freeze drying caused a further 25% loss of oxygen. The product, a colourless viscous liquid containing 80% permonophosphoric acid, slowly lost oxygen if allowed to stand at room temperature. Unstable amorphous lithium, sodium or potassium salts were obtained by neutralization with the appropriate hydroxide, and evaporation of the resulting solution *in vacuo*.[39]

## Properties

*Peroxomonophosphoric acid*, $H_3PO_5$, a strong oxidizing agent, liberates iodine from acidified potassium iodide solution and oxidizes manganous salts, in the cold, to permanganate. Although stable in concentrated aqueous and acetonitrile solutions, it is said to hydrolyze in dilute solution to form orthophosphoric acid and hydrogen peroxide,[7–8] according to equation (iv):

(iv) $$H_3PO_5 + H_2O \rightleftharpoons H_3PO_4 + H_2O_2$$

The kinetics of this decomposition have been studied in aqueous alkaline media, ethylenediaminetetraacetic acid being added to suppress homogeneous catalysis by trace metal ions. The bimolecular decomposition had a maximum rate near pH 12·5, corresponding closely to the third dissociation constant of the acid, which the authors determined as $pK_{3a} = 12{\cdot}8 \pm 0{\cdot}2$. It is therefore suggested that under these conditions decomposition occurs by nucleophilic attack of the species $PO_5^{3-}$ on the phosphorus atom of a second $HPO_5^{2-}$ ion.[33]

This was confirmed in a study of the decomposition of $H_3PO_5$ by alkali containing $^{18}O$ at 20°C. In acid solutions, however, a different mechanism obtains.[40] The hydrolysis is of first order in peroxo acid, and also depends (but not linearly) on pH. Rate constants, activation parameters and other data suggest a mechanism involving nucleophilic attack of water on a protonated species:

$$H_3PO_5 + H^+ \rightleftharpoons H_4PO_5^+$$
$$H_4PO_5^+ + H_2O \rightarrow H_3PO_4 + H_2O_2 + H^+$$

The rate of hydrolysis is accelerated tenfold by 0·1 M. fluoride ion, probably by a bimolecular nucleophilic displacement mechanism.[41]

A study of possible isotope exchange between radioactive phosphate and peroxomonophosphoric acid, prepared by the method of reference 4, was prevented by difficulties encountered in the separation of the two species, during which complete decomposition of the peroxo-ion occurred.[9]

After neutralization, solutions of peroxomonophosphoric acid give a dark precipitate with silver nitrate, which rapidly turns white and in a few hours becomes yellow, owing to the formation of silver orthophosphate, which is accompanied by the evolution of ozonized oxygen. Precipitates formed in alkaline solution by silver, iron, nickel and manganous salts rapidly change to orthophosphates, again with evolution of ozonized oxygen.[1]

*Peroxodiphosphoric acid*, $H_4P_2O_8$, on the other hand is more stable in dilute solution, possibly because it has first to hydrolyze to peroxomonophosphoric acid by the reaction given in equation (iii), and liberates iodine only slowly from an iodide solution, the rate depending sensitively on the acidity of the system.[30] A later kinetic study of this reaction has indeed shown that the reaction takes three main paths:

$$H_3P_2O_8^- + I^- \rightarrow HPO_4^{2-} + H_2PO_4^- + I^+$$
$$H_3P_2O_8^- + H_2O \rightarrow H_2PO_4^- + H_2PO_5^- + H^+$$
$$H_2P_2O_8^{2-} + I^- \rightarrow 2HPO_4^{2-} + I^+$$

These are followed by fast reactions which give the final products.[42]

Accurate volumetric determination of the peroxodiphosphate ion in acid solution by the addition of excess of ferrous sulphate followed by back-titration with potassium chromate solution has been described[30] and direct potentiometric titration of acid peroxodiphosphate solutions with ferrous ammonium sulphate is also possible.[30] In the oxidation of tris(1,10-phenanthroline)iron(II), the rate-determining step is the dissociation of the Fe(II) complex ion.[43]

The manganous ion can be oxidized quantitatively to manganese dioxide, slowly at room temperature and rapidly at 100°C., by excess of peroxodiphosphate[3]; the permanganate ion is thought to be an intermediate in the reaction mechanism. Incomplete oxidation of thallous, chromic and cobaltous ions and selenic acid occurs under the same conditions, but the oxidation of the thallous and chromic ions was found to be quantitative in the presence of known amounts of manganous ion.[3] The oxidation-reduction potentials of $P_2O_8^{4-}$ and $PO_5^{3-}$ solutions have been measured, using smooth and platinized platinum electrodes against the standard calomel electrode. The substances which determined the oxidation-reduction potential of $P_2O_8^{4-}$ were its decomposition products, especially $PO_5^{3-}$. The potential for $PO_5^{3-}$ depended linearly on the logarithm of the concentration of $PO_5^{3-}$. Hydrogen peroxide caused a lowering of the potential.[44]

It has been reported[10] that the peroxodiphosphate ion decomposes more slowly in $H_2{}^{18}O$ than percarbonate or perborate ions, and that the origin of the oxygen formed depends on the pH of the solution. For example, at pH 5·2, 81% of the oxygen formed was derived from the peroxodiphosphate ion, whilst at pH 12·8 all was derived from water. At room temperature no $^{18}O$ was exchanged between $H_2{}^{18}O$ and potassium peroxodiphosphate in 8 hr.

Acid hydrolysis of the peroxodiphosphoric acid,[11] or other peroxopolyphosphoric acid components of the reaction products obtained, for example, by the reaction between hydrogen peroxide and phosphoric oxide suspended in phosphoric acid[5] for a short period at temperatures not exceeding 60°C., considerably increases the proportion of peroxomonophosphoric present.

The hydrolysis of peroxomono- and peroxodi-phosphates has been reported to be similar to that of pyrophosphates.[45] A study of the hydrolysis over a pH range 0–7·6 and a range of ionic strengths 1·6-3·8 showed, however, that the kinetics were complex, and could be explained only if the variously protonated ions of peroxodiphosphate each had a specific velocity constant for its hydrolysis. Because of the complexity of the system, the nature of the transition state complex could not be deduced from these kinetic data, and hence the authors could not distinguish between the possibilities:

$$(1a) \qquad H_nP_2O_8^{(n-4)-} + H^+ \rightleftharpoons H_{n+1}P_2O_8^{(n-3)-}$$

$$(1b) \qquad H_{n+1}P_2O_8^{(n-3)-} + H_2O \rightarrow \text{products}$$

$$(2) \qquad H_nP_2O_8^{(n-4)-} + H_3O^+ \rightarrow \text{products}^{46}$$

The addition of thiocyanates increases the oxidizing power of peroxophosphates in electrolytic cells by the fixation of pseudocyanogen on the anode, which prevents active centres from catalyzing the formation of gaseous oxygen. The effect decreases with decreasing pH and is less for peroxophosphates than for persulphates, but greater than for perborates.[12]

## PEROXOPHOSPHATES

### Preparation and Properties

Several general methods are available for the preparation of peroxophosphates:

(*a*) neutralization of solutions of the peroxoacids with bases,
(*b*) anodic oxidation of suitable electrolytes,
(*c*) precipitation and double decomposition reactions.

(*a*) Solutions of the alkali metal, ammonium, magnesium or calcium salts of peroxomonophosphoric acid can be obtained in a comparatively pure state by neutralization, with the appropriate bases, of a concentrated solution of the acid prepared as described in references 5 and 11. On evaporation *in vacuo* at low temperature, or on the addition of water-miscible solvents, such solutions yield the crystalline salts.[11]

(*b*) Alkali metal and ammonium salts of peroxophosphoric acids can also be prepared by the anodic oxidation of phosphates; the yields obtained by the methods reported earlier[1] can be improved by adding small amounts of chromates and fluorides to the electrolyte, or by keeping the temperature low and using an anode current density not exceeding 0·020 amp./cm.[2, 13–5] Crude ammonium perphosphate made by this process may contain chromate, which is difficult to remove by recrystallization. However, metathesis with sodium perchlorate gives sodium permonophosphate which is more readily purified.[42]

As the formation of peroxophosphoric acid when fluorine is bubbled through orthophosphoric acid has been reported,[16] it was suggested that fluorine might be an intermediate in the mechanism of anodic oxidation in the presence of fluorides,[13] for example as illustrated by equations (v) and (vi):

$$\text{(v)} \qquad 2K_2HPO_4 + F_2 = K_4P_2O_8 + 2HF$$

$$\text{(vi)} \qquad K_4P_2O_8 + H_2O = K_2HPO_5 + K_2HPO_4$$

The formation of the peroxomonophosphate is minimized by performing the electrolysis under alkaline conditions; for example the electrolysis, at 10°C., of a solution containing 302 g. of potassium dihydrogen orthophosphate, 198 g. of potassium hydroxide, 120 g. of potassium fluoride and 0·355 g. of potassium chromate per litre, using a platinum dish as anode, a rotating platinum rod as cathode and a current density of 0·023 amp./cm.$^2$, gives up to 85% conversion to potassium peroxodiphosphate, which may be obtained by a single crystallization from the aqueous solution in purities up to 90% $K_4P_2O_8$[13, 17] and practically pure by three-fold recrystallization.

The yield of peroxophosphates is not enhanced by carrying out the electrolysis under specific conditions in the presence of a glow-discharge,[14] as is that of hydrogen peroxide from potassium hydrogen phosphate.[9] Optimum concentrations, pH and temperatures have been given for $H_4P_2O_8$ production. The current yield is good and increases with increasing over-voltage of the anode metal. Yields are diminished by addition of fluorides.[47]

(*c*) When soluble salts of barium, zinc or lead are added to aqueous solutions of potassium peroxodiphosphates, the following compounds are precipitated[13]:

$Ba_2P_2O_8,4H_2O$, a white micro-crystalline solid, slightly soluble in water, easily soluble in nitric or hydrochloric acid.
$Zn_2P_2O_8,4H_2O$, a white micro-crystalline precipitate, fairly soluble in water.
$Pb_2P_2O_8$, a heavy white precipitate, insoluble in water.

No precipitate is formed when magnesium sulphate solution or magnesia mixture is added to aqueous potassium peroxodiphosphate, and this observation affords a method of separating phosphate from peroxophosphate[13] in solution.

A colourless silver salt, $Ag_4P_2O_8$, is precipitated when potassium peroxodiphosphate reacts with silver nitrate in saturated ammonium nitrate at −14°C.,[18] but it quickly decomposes on standing according to reaction (vii):

$$\text{(vii)} \qquad 3Ag_4P_2O_8 + 3H_2O = 4Ag_3PO_4 + 2H_3PO_4 + 3O$$

By double decomposition with salts of perchloric acid, neutral and acid sodium and ammonium peroxodiphosphates can be prepared from the potassium salt[19] according to reactions of the type illustrated in equations (viii) and (ix):

$$\text{(viii)} \qquad K_4P_2O_8 + 4NaClO_4 = Na_4P_2O_8 + 4KClO_4$$

$$\text{(ix)} \qquad K_4P_2O_8 + 2HClO_4 + 2NaClO_4 = Na_2H_2P_2O_8 + 4KClO_4$$

the products being separated by fractional crystallization.

Tertiary butyl dialkyl esters of permonophosphoric acid have been made by the action of *tert.* butyl peroxide on dialkyl phosphorochloridates:

$$(RO)_2POCl + Me_3COOH = (RO)_2P(O)OOCMe_3 + HCl$$

They are moderately stable solids, but the corresponding aryl esters deflagrated on isolation.[34]

Thermal decomposition of the alkyl esters gives 55–80% yields of tetraalkyl pyrophosphates[48]:

$$(RO)_2POOOCMe_3 \rightarrow ((RO)_2PO)_2O \quad \text{etc.}$$

Although the preparation of peroxomonophosphates has been reported,[49] little has been recorded of their properties; more is known about the formation and behaviour of peroxodiphosphates, for example:

*Neutral potassium peroxodiphosphate*, $K_4P_2O_8$, is very soluble in water, but crystals can be separated by slow concentration over sulphuric acid of electrolytes resulting from anodic oxidation of the orthophosphate. Stored in well-stoppered bottles the crystalline salt is stable.[13,17] The oxidation of freshly reduced solutions of leuco-malachite green and leuco-indigo by potassium peroxodiphosphate occurs slowly at room temperature, but instantly in the presence of a trace of silver nitrate,[13] the catalytic effect of which is possibly due to the decomposition reaction (equation vii).

*Acid potassium peroxodiphosphate* has been prepared[19] by the dropwise addition of an aqueous solution of perchloric acid to a well-stirred neutral potassium peroxodiphosphate solution, both solutions being ice-cold:

$$K_4P_2O_8+2HClO_4 = 2KClO_4+K_2H_2P_2O_8$$

After removal of the relatively insoluble potassium perchlorate, the acid perdiphosphate is precipitated by the addition of methanol. Crystallization from a water–methanol solvent gives phosphate-free, colourless needles, readily soluble in water with a composition corresponding to $K_2H_2P_2O_8$. Being free from chromate and phosphate, it is a useful source for the preparation of the neutral salt for spectroscopic standards.[19]

The primary and tertiary salts have not been reported.

*Neutral sodium peroxodiphosphate* is more readily prepared by double decomposition, according to equation (iv), than by direct anodic oxidation of sodium orthophosphate.[19] After separation of the less soluble potassium chlorate, recrystallization of the crude product from water yields pure $Na_4P_2O_8,20H_2O$ in the form of colourless hexagonal plates moderately soluble in water, the solution being weakly alkaline. On exposure to air at room temperature the crystals rapidly effloresce to the hexahydrate $Na_4P_2O_8,6H_2O$. Tensimetric measurements[19] show the existence of $Na_4P_2O_8,18H_2O$, and also indicate that the hexahydrate exists in two forms, one of which changes into a second unstable form between 30° and 40°C. The transition is accelerated by the presence of the unstable phase and rapid decomposition thus ensues.

*Acid sodium peroxodiphosphate* is prepared from the neutral potassium salt by double decomposition under ice-cold conditions, according to equation (ix), the perchloric acid being added first, followed by the sodium perchlorate solution. After purification by recrystallization, colourless prisms, moderately soluble in water, with the composition $Na_2H_2P_2O_8,2H_2O$ are formed.[19]

*Neutral ammonium peroxodiphosphate* is obtained in good yield by electrolysis,[13,15] but is not easily separated from solution in the solid state, since the ammonium ion is liable to undergo oxidation by the $P_2O_8^{4-}$ ion to form ammonium phosphate and ammonium nitrate.[13] However, the double decomposition technique using ammonium perchlorate, when carried out under well-controlled, ice-cold conditions, gives colourless crystals with the composition $(NH_4)_2P_2O_8,2H_2O$.

*Acid ammonium peroxodiphosphate* is obtained[19] as described for the corresponding sodium salt, using ammonium instead of sodium perchlorate. The compound $(NH_4)_2H_2P_2O_8$ crystallizes as colourless needles readily soluble in water and having an acid reaction.

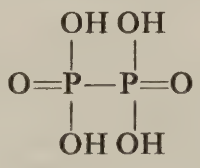
The peroxophosphates of rubidium and cæsium are more easily prepared by anodic oxidation than those of potassium, even without fluorides or chromates being present.[13,15] Lithium peroxodiphosphate, $Li_4P_2O_8,4H_2O$, derived from the potassium salt by a double decomposition reaction with lithium perchlorate,[30] is thought on the basis of nuclear magnetic resonance evidence to have a symmetric structure.[3] Potentiometric and conductimetric titrations also revealed that the corresponding acid possesses one strongly dissociated hydrogen atom per phosphorus atom, which suggests the presence of the –P–O–O–P– group in the molecule.[3]

## Ionization Constants and Structures

The pH titration curves of tetramethylammonium peroxodiphosphate against hydrochloric acid at 25°C., a typical example of which is shown in Fig. 1, have been obtained at a series of ionic strengths, and give figures for the third and fourth ionization constants[20] which on extrapolation to infinite dilution yield the values: $K_3 = 6{\cdot}6 \pm 0{\cdot}3 \times 10^{-6}$; $K_4 = 2{\cdot}1 \pm 0{\cdot}1 \times 10^{-8}$.

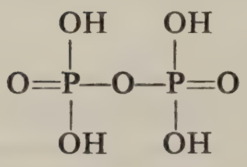
Approximate values for the first and second ionization constants, deduced from the trends observed in other tetrabasic acids of similar structure (see Fig. 2) are: $K_1 \simeq 2$; $K_2 \simeq 3 \times 10^{-1}$.

The three related phosphorus acids referred to in Fig. 2 may be represented by the following structures:



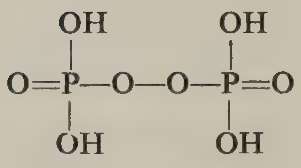
$$\mathrm{O{=}\underset{OH}{\overset{OH}{P}}{-}\underset{OH}{\overset{OH}{P}}{=}O}$$

hypophosphoric acid



$$\mathrm{O{=}\underset{OH}{\overset{OH}{P}}{-}O{-}\underset{OH}{\overset{OH}{P}}{=}O}$$

pyrophosphoric acid



$$\mathrm{O{=}\underset{OH}{\overset{OH}{P}}{-}O{-}O{-}\underset{OH}{\overset{OH}{P}}{=}O}$$

peroxodiphosphoric acid

the first two of which have been established by physical methods, whilst that of the peroxoacid is generally accepted. It has been suggested[20] that the increasing acid strength, in the order hypo-, pyro- and peroxo-acids, may be attributed to the increasing electro-negativity of the additional oxygen atoms attached to the phosphorus along the series; this facilitates the removal of hydrogen ions, by decreasing the electron density at the hydrogen atoms. It may also be supposed that inductive effects, due to intramolecular charges, decrease as the central P atoms become further separated.

The values of the formation constants of complex ions of peroxodiphosphoric acid with cations, e.g. $Li^+$, $K^+$, $Mg^{2+}$, compared with the constants of the complex ions of these metals with pyrophosphoric acid, support the structural configuration proposed above for the peroxoacid.[20] The Raman and infra-red spectra of potassium, sodium and ammonium peroxodiphosphates are also in conformity with a structure of this type, in which the two phosphorus atoms are in a *trans* configuration to one another.[35]

A polarographic method has been described for the determination of peroxo-, mono- or di-phosphates, separately or together.[36]

Although not definitely established, it is considered likely from their chemical and physical properties[20] and by analogy with the peroxosulphates, that the various peroxophosphate ions reported have the structures illustrated below (Fig. 3). Others,

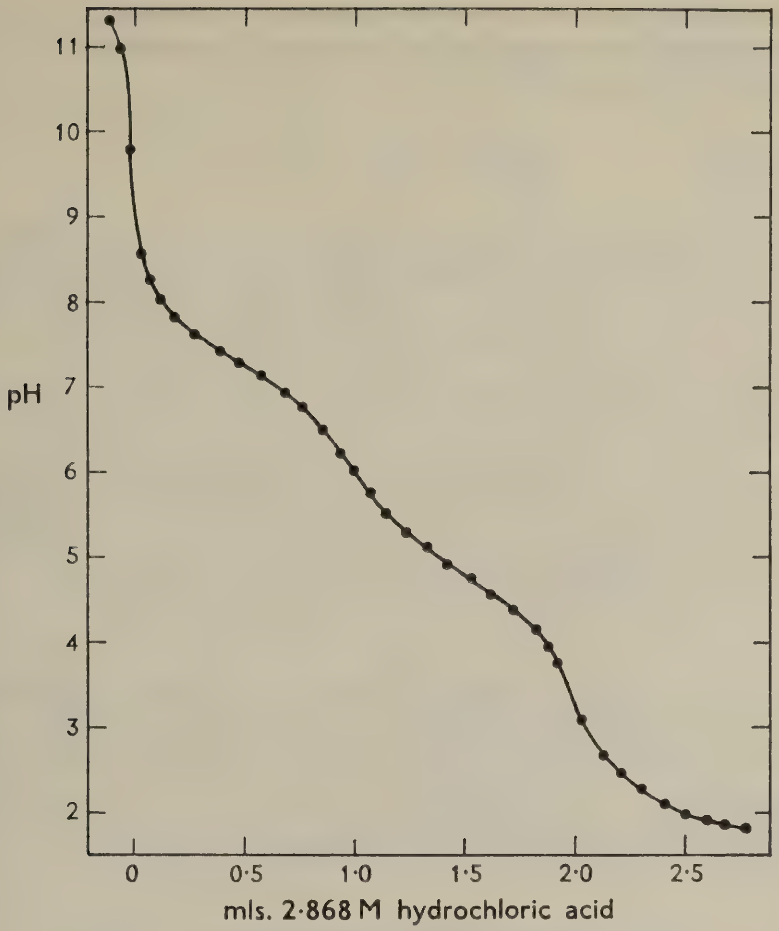


FIG. 1.—Titration curve for the peroxodiphosphate ion

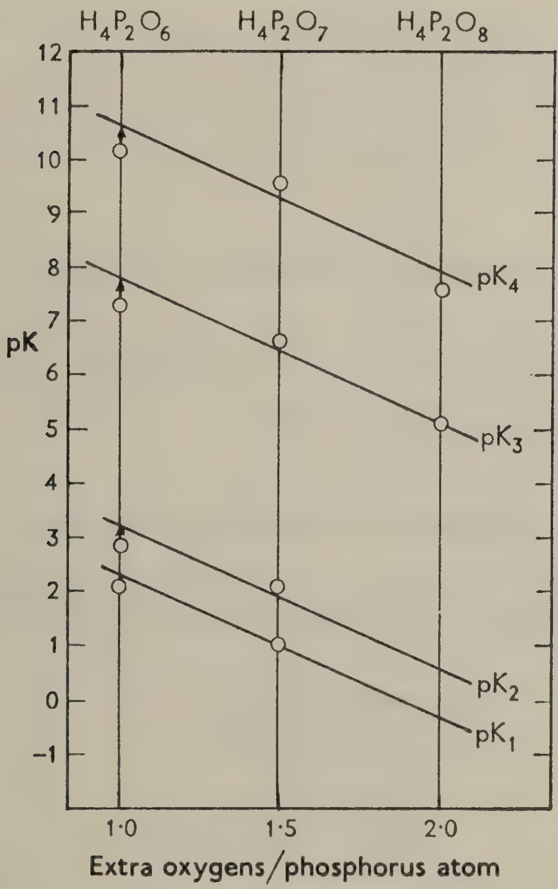
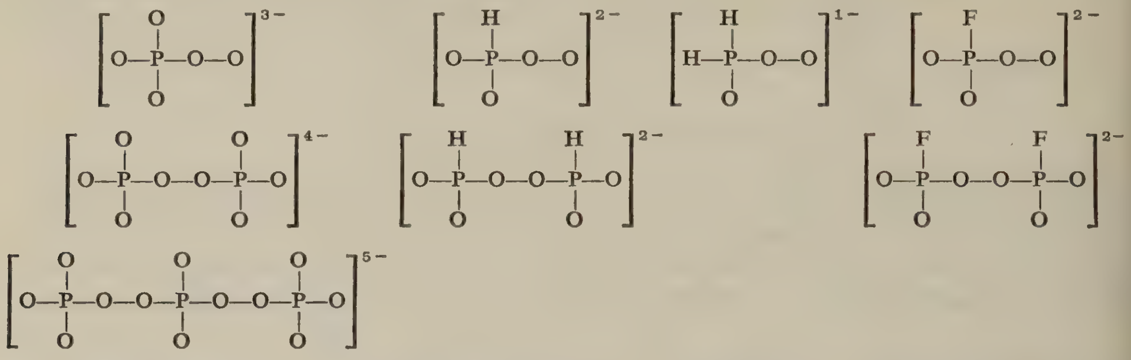


FIG. 2.—The effect of structure on the acidity of three related phosphorus acids

more complex, or (less probably) with phosphorus in a lower valency state, can be visualized, for example the hypothetical peroxopolyphosphoric and the peroxohypophosphorous ions formulated in Fig. 3.



Peroxomono-, di- and (tri-) phosphate ions

Peroxomono- and diphosphite ions

Peroxomono-hypophosphite ion

Peroxomono-fluoromono-phosphate and peroxodifluoro-diphosphate ions

FIG. 3.—Probable structures of the peroxophosphate ions

## Uses

The practical application of peroxophosphates has received little study so far, but they have been suggested as detoxicants for hydrogenation catalysts which have been poisoned by sulphur compounds, such as cysteine, $\beta$-thionaphthol, thiophen[24-5] or carbon disulphide,[26] or by phosphorus compounds such as dimethylphenylphosphine.[27] Desorptive washing of the poisoned platinum catalyst by the peroxophosphate solution restores its activity to the original value.

## PEROXOPHOSPHITES

When sodium hypophosphite or phosphite is oxidized in dilute aqueous solution with oxygen containing a little ozone or fluorine, the presence, in solution, of compounds which have oxidizing properties resembling those of the peroxophosphates has been reported.[21] Peroxomono- and peroxodiphosphorous acids have been suggested as intermediates in the chain mechanism proposed for this autoxidation reaction.

## PEROXOFLUOROPHOSPHATES

Anodic oxidation of alkali metal or ammonium salts of monofluorophosphoric acid, or of the acid itself, is believed to form peroxofluorophosphoric acids or salts analogous to the peroxophosphoric acids already described.[22-3] These compounds are also discussed in Section XXX.

## PHOSPHATE PEROXOHYDRATES

A number of neutral or alkaline phosphates form compounds with hydrogen peroxide, in which the $H_2O_2$ molecule takes the place of water of hydration[15, 28-9, 50] for example:

$Na_3PO_4,2H_2O_2$
$Na_2HPO_4,2H_2O_2$
$K_4P_2O_7,3H_2O_2$
$Na_4P_2O_7,2H_2O_2$
$Na_4P_2O_7,2H_2O_2,8H_2O$
$Na_5P_3O_{10},2H_2O_2,H_2O$

On solution in water these compounds quickly yield hydrogen peroxide and do not therefore oxidize iodides as rapidly as the salts of the true peroxophosphoric acids themselves. They are generally prepared by mixing concentrated hydrogen peroxide with the respective anhydrous salts.

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### SECTION XXX

# THIOPHOSPHOROUS AND THIOPHOSPHORIC ACIDS AND THEIR SALTS

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## THIO-ORTHOPHOSPHORIC ACIDS

ALTHOUGH many salts of the phosphorus thio-acids have been prepared (Mellor, VIII, 1061–71), the acids themselves have not been studied extensively. This may be due to the belief that they all decompose spontaneously in solution.[1-3] Dithiophosphoric acid, $H_3PO_2S_2$, and monothiophosphoric acid, $H_3PO_3S$, were discovered in an attempt to prepare tetrathiophosphoric acid, $H_3PS_4$, from barium tetrathiophosphate, $Ba_3(PS_4)_2,12H_2O$, by treatment with acid.[4] Any tetrathiophosphoric acid formed is hydrolyzed at once:

$$H_3PS_4+H_2O = H_3POS_3+H_2S$$

The trithio-acid is also unstable in solution:

$$H_3POS_3+H_2O = H_3PO_2S_2+H_2S$$

Dithiophosphoric acid is more stable and can be detected in solution. It is more slowly hydrolyzed to the relatively stable monothiophosphoric acid.

### Preparation and Properties of Free Thiophosphoric Acids

Monothiophosphoric acid (phosphorothioic acid, $H_3PO_3S$) is best prepared from barium dithiophosphate and sulphuric acid. By using this salt the amount of hydrolysis of the monothiophosphoric acid ultimately formed is greatly reduced. A 5% solution of the acid can be obtained; this decomposes very slowly on standing, evolving hydrogen sulphide and, if air is present, depositing sulphur. The pure acid may be obtained by ion-exchange removal of pyridine from its pyridinium salt, and freeze-drying of the eluate.[5] The monohydrate, $H_3PO_3S,H_2O$, is the final product.

The acid decomposes very slowly below room temperature; less than 10% of a 3·6% solution in water decomposes after 8 weeks at −2°C. If water is distilled under vacuum from a 5% solution at 0°C. an oily liquid containing *ca.* 84% $H_3PO_3S$, sp. gr. 1·7, remains. On further cooling it solidifies at −60° to a glass. If the liquid is warmed to 50°, hydrogen sulphide is vigorously evolved. The acid solution cannot be made more concentrated than 84% under these conditions.

Monothiophosphoric acid reduces ferricyanide in a mole-for-mole ratio, forming a phosphorothioate dimer. The kinetics of the reduction are of second order with respect to the reactants over the pH range 5·8–7·8 (ionic strength $\mu = 0{\cdot}035$–$0{\cdot}06$, temperature 15°–40°) and the rate constant shows a minimum at pH 6·2. Free radical intermediates were demonstrated. From a potentiometric titration of trisodium thiophosphate against N. hydrochloric acid at 23°, three apparent dissociation constants were evaluated: $pK_1 < 2$, $pK_2 = 5{\cdot}75$, $pK_3 = 10{\cdot}4$.[68]

Monothiophosphoric acid is also the end-product of the hydrolysis of thiophosphoryl fluoride, $PSF_3$, which is believed to occur in stages:

$$PSF_3 \rightarrow HPOSF_2 \rightarrow H_2PO_2SF \rightarrow H_3PO_3S$$

Dithiophosphoric acid (phosphorodithioic acid, $H_3PO_2S_2$) may be prepared by acidifying barium tetrathiophosphate, $Ba_3(PS_4)_2$, or barium dithiophosphate, the former being preferable.[4] If the dithio-salt is used, considerable hydrolysis of the dithiophosphoric acid formed occurs during the preparation. Even when barium tetrathiophosphate is used the preparation must be carried out in saturated hydrogen sulphide solution at 0°C. to suppress hydrolysis. Rapid neutralization of the acid solution with sodium hydroxide solution gives a sodium salt, the crystal form and *X*-ray diagram of which are characteristic of sodium dithiophosphate. A 2·3% solution of dithiophosphoric acid hydrolyzes completely to monothiophosphoric acid in 10 hr. at 0°C.[4]

Tetrathiophosphoric acid (phosphorotetrathioic acid, $H_3PS_4$) is prepared by treating sodium tetrathiophosphate with hydrochloric acid and pouring the vigorously stirred mixture into acetone at −70°C. Yields as high as 96% were claimed.[6−7]

The rate of hydrolysis of monothiophosphoric acid has been studied in detail; a plot of the observed rate constant *vs.* pH gives a bell-shaped curve with a rate maximum of $1{\cdot}64\times10^{-4}$ sec.$^{-1}$ at 52·8°C. and pH 3·0. Another rate maximum is observed at pH 8.[8] The rate constants for hydrolysis of the acid at 52·8° in a solution of 1 M. ionic strength are $2{\cdot}43\times10^{-5}$ sec.$^{-1}$ for the neutral acid, $16{\cdot}7\times10^{-5}$ sec.$^{-1}$ for the monoanion, $3{\cdot}81\times10^{-5}$ sec.$^{-1}$ for the dianion and $1{\cdot}56\times10^{-5}$ sec.$^{-1}$ the trianion.[9]

Monothiophosphoric acid is oxidized by iodine in solution. The reaction course is probably[10]:

$$2[H_2PO_3S]^- + I_2 \rightleftharpoons [HPO_3S\text{–}SPO_3H]^{2-} + 2I^- + 2H^+$$

No physical measurements appear to have been made on trithiophosphoric acid, which is rapidly hydrolyzed in solution. Tetrathiophosphoric acid is even more unstable, and has been reported to have a half-life of about 20 min. at 20°C.[11] In both cases the final product of hydrolysis is monothiophosphoric acid.

The sulphur content of the thiophosphoric acids may be determined by treatment with excess of iodine in alkaline solution and back-titration of the acidified solution with thiosulphate. Phosphorus can be determined as ammonium phosphomolybdate by the Lorenz method.[4]

## THIOPHOSPHATES

There are two basic routes for the preparation of salts of the thiophosphoric acids. One uses a starting material, such as a thiophosphoryl halide or phosphorus sulphide, which already contains P–S bonds, and the other involves the formation of P–S bonds in the course of the preparation.

### Monothiophosphates

Trisodium monothiophosphate dodecahydrate (trisodium phosphoromonothioate, $Na_3PO_3S,12H_2O$) has been prepared by refluxing thiophosphoryl chloride, $PSCl_3$, with aqueous sodium hydroxide.[12−3] When the mixture is cooled in ice the solid thiophosphate separates out and can be filtered off and reprecipitated from aqueous solution with methanol. Thiophosphoryl fluoride can also be used as starting material.[14] The anhydrous salt is obtained when the hydrated salt is suspended in anhydrous methanol; after an hour the crystals are filtered off and heated at 100°C. for 1 hr.[12] Sodium monothiophosphate has also been prepared by heating a finely powdered 1 : 1 mixture of sodium metaphosphate and anhydrous sodium sulphide to 750°C. in an atmosphere of nitrogen, or *in vacuo*[15]:

$$NaPO_3 + Na_2S = Na_3PO_3S$$

*X*-ray studies show that the product of this reaction is identical with that obtained from alkaline hydrolysis of thiophosphoryl chloride.[15] The product is only 87% pure since water in the metaphosphate takes part in the reaction:

$$H_2O + Na_2S + NaPO_3 = Na_3PO_4 + H_2S$$

Sodium hydroxide and sodium carbonate in the sulphide also yield phosphate:

$$2NaOH + Na_2S + 2NaPO_3 = 2Na_3PO_4 + H_2S$$
$$Na_2CO_3 + NaPO_3 = Na_3PO_4 + CO_2$$

The impurities may be precipitated from a solution of the crude thiophosphate by careful addition of magnesium sulphate solution, avoiding an excess of the reagent, which redissolves the precipitate. Good yields of sodium monothiophosphate can also be obtained by the action of sodium trithiocarbonate on metaphosphates, particularly sodium trimetaphosphate.[61] Trisodium monothiophosphate dodecahydrate can be recrystallized from aqueous alcohol.[15]

The solubility of the hydrate in water is given in Table I.[12]

*Table I.—Solubility of Trisodium Monothiophosphate Dodecahydrate in Water*

| Temperature °C. | Solubility g./l. |
|---|---|
| 4 | 21·2 |
| 18 | 79·2 |
| 28 | 132·7 |
| 38 | 241·5 |

The crystals of trisodium monothiophosphate dodecahydrate are rhombic, with parameters $a = 12{\cdot}58$ A., $\alpha = 42{\cdot}3°$. [16] There does not appear to be any mixed crystal formation between the thiophosphate and the corresponding phosphate, $Na_3PO_4,12H_2O$; the *X*-ray diffraction pattern of each component appears to be unaffected by the presence of the other.

The positions and intensities of the bands in the infra-red spectrum of the dodecahydrate are given in Table II.[17]

*Table II.—Infra-red Absorption Frequencies (cm.$^{-1}$) of Trisodium Monothiophosphate Dodecahydrate*

| | | | |
|---|---|---|---|
| 3430 | s | 1068 | s |
| 1642 | m–w | 988 | vw |
| 1252 | w | 952 | m–s |
| 1157 | m–s | 860 | m–s |
| ~1125 | m–s | | |

The infra-red spectra of trisodium monothiophosphate and its dodecahydrate are given in Figs. 1 and 2.[18]

At room temperature the solid hydrate smells slightly of hydrogen sulphide, indicating slow decomposition; at 60°C. decomposition is rapid.[12] Investigation of the thermal behaviour of the salt using the techniques of thermogravimetry and differential thermal analysis shows that an endothermic change occurs at *ca.* 48°C. corresponding to the transformation[18]:

$$Na_3PO_3S,12H_2O = Na_3PO_3S,9H_2O + 3H_2O$$

At 64°C. the nonahydrate dissolves in its own water of crystallization, at the same time undergoing partial hydrolysis. The subsequent dehydration to the anhydrous salt is reversible and if the anhydrous salt is kept in a current of nitrogen saturated with water vapour at *ca.* 20°C., it takes up water rapidly to form the nonahydrate which then slowly changes to the dodecahydrate.[18]

Anhydrous trisodium monothiophosphate is very stable at room temperature, and does not decompose when heated to 100°C. in air. It does not absorb moisture from the air at relative humidities below 31%.[12] The salt is stable in oxygen up to 296°C. At this temperature the P–S bond is broken in a highly exothermic reaction involving the formation of phosphate, pyrophosphate, sulphur dioxide, sulphate and elemental sulphur.[18] If the anhydrous salt is heated *in vacuo* there is no evolution of sulphur dioxide, but slow liberation of sulphur begins at *ca.* 300°C., decomposition being complete only at 800°C. The residue contains sodium sulphide and compounds containing phosphorus in a low oxidation state.[18]

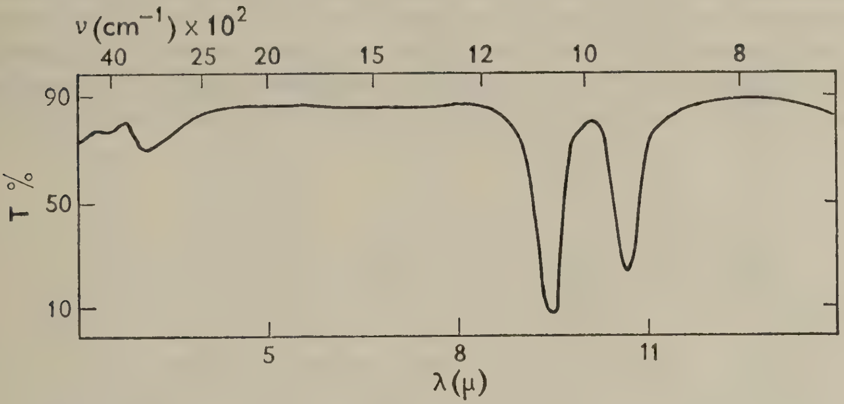


FIG. 1.—Infra-red spectrum of anhydrous trisodium monothiophosphate

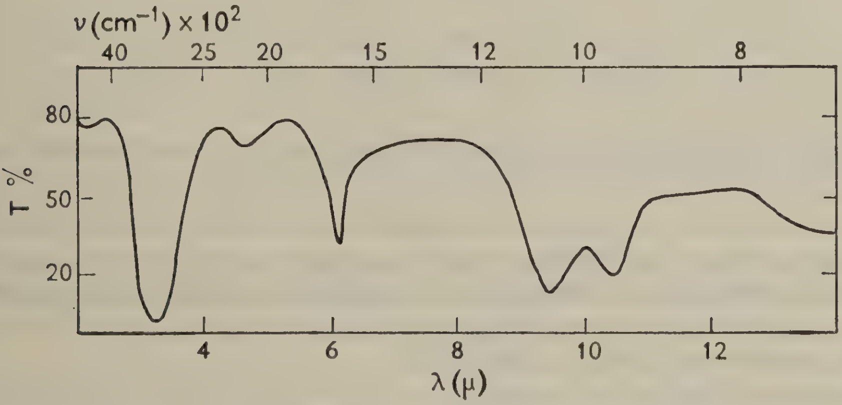


FIG. 2.—Infra-red spectrum of trisodium monothiophosphate dodecahydrate

Aqueous solutions of trisodium monothiophosphate decompose very slowly at room temperature[61]; addition of sodium carbonate stabilizes the solution. Acidification of the solution gives the disodium salt, which is rapidly hydrolyzed to monothiophosphoric acid,[18] and finally to phosphoric acid.[19] The rate constant for hydrolysis of trisodium monothiophosphate in 1 M. sodium hydroxide at 50°C. has been determined as $2{\cdot}5 \times 10^{-4}$ min.$^{-1}$; silicone grease catalyzes the reaction, increasing the rate constant to $2{\cdot}1 \times 10^{-3}$ min.$^{-1}$.[20] Acid titration of a solution of trisodium monothiophosphate with a glass electrode gives two well defined waves at 25°, with p*K* values roughly 10·2 and 5·6.[21]

If a lead salt is added to a solution of trisodium monothiophosphate a white precipitate forms, which on warming rapidly turns black through formation of lead sulphide. This reaction may be used to determined the purity of crude trisodium monothiophosphate; the sulphur content may be determined by titration with alkaline iodine solution[15]:

$$Na_3PO_3S+4I_2+10NaOH = Na_3PO_4+8NaI+Na_2SO_4+5H_2O$$

An attempt has been made to prepare a trisodium salt, $NaS.PO(ONa)_2$, as a compound distinct from $NaO.PS(ONa)_2$, starting with trimethyl phosphoromonothionate, $PS(OCH_3)_3$.[22] Monosodium dimethyl and disodium monomethyl monothiophosphates were isolated and characterized, but no salt differing from trisodium monothiophosphate was identified.

If concentrated hydrochloric acid is dropped into an aqueous solution of trisodium monothiophosphate at 10°C., and the mixture is then cooled to 0°C. and treated with alcohol, an oil appears. This oil crystallizes on being stirred with acetone and cooled in an ice–salt mixture. The composition $Na_2HPO_3S,5H_2O$ was attributed[4,18] to these crystals which were very hygroscopic. Their infra-red spectrum is given in Fig. 3.

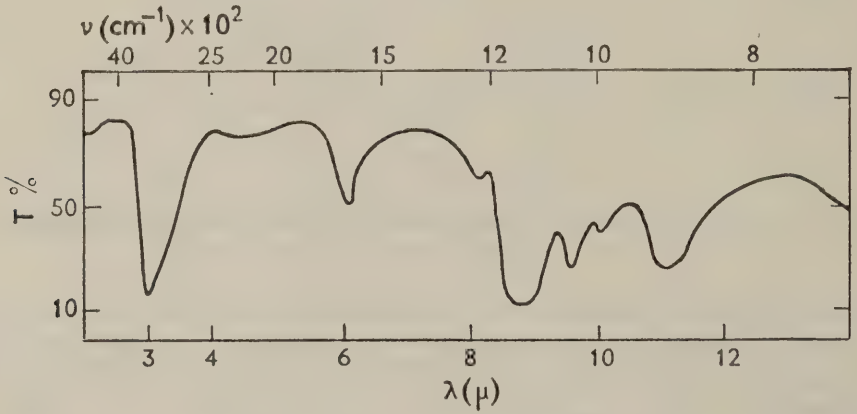


FIG. 3.—Infra-red spectrum of disodium monothiophosphate pentahydrate

A fairly pure sample of anhydrous disodium monothiophosphate has been obtained by dehydrating the hydrate over phosphoric acid in a desiccator.[23] The infra-red band positions and intensities for the hydrated disodium monothiophosphate in potassium bromide discs, and the Raman band positions and intensities for an aqueous solution are given in Table III.[23]

In an improved method of preparation of disodium monothiophosphate the treatment with alcohol was accompanied by scratching, and the salt was precipitated in the reaction solution.[24] This product was shown to be the hydrate, $Na_2HPO_3S$, $6{\cdot}5H_2O$. It was stable in air for a short period, but yielded the phosphate in 1–2 days. Hydrogen sulphide is evolved when this salt is heated to 40°C., and at 50°C. a clear melt is obtained.[24]

Trisodium monothiophosphate can be detected by liberation of iodine after paper chromatographic separation in quantities as small as 0·6 μg. (using perchloric/periodic acid medium) and 0·2 μg. (using iodine/sodium azide medium).[25] Paper-chromatographic spots developed with an aqueous solution of sodium fluoresceinate and silver nitrate appear green in visible light and dark under ultra-violet light.[26]

Potassium monothiophosphate has been prepared by hydrolyzing thiophosphoryl chloride with potassium hydroxide solution under reflux and cooling the product in an ice bath. The salt is purified by repeated crystallization from methanol. It is difficult to remove all traces of potassium chloride, possibly because it is slightly soluble in a methanol–water mixture.[12] The potassium salt forms no hydrate.

Wedge-shaped crystals of the monopotassium salt, $KH_2PO_3S$, are precipitated by methanol–ether from an aqueous solution prepared by neutralizing monothiophosphoric acid to pH 4·5 with potassium hydroxide, while at pH 9 the dipotassium salt, $K_2HPO_3S$, can be isolated.[62]

When thiophosphoryl chloride is refluxed with concentrated aqueous ammonia only phosphate and ammonium chloride are obtained as the reaction products.

*Table III.—Infra-red and Raman Absorption Frequencies (cm.$^{-1}$) for Disodium Monothiophosphate*

| $Na_2HPO_3S$,aq. in KBr | $Na_2HPO_3S$ in aqueous solution |
|---|---|
| | 369/389 vw |
| | 438 w |
| 490 vw | |
| 525 vw | |
| 620 s | 610$\pm$10 s |
| (720 vw) | 701 m |
| 860 m | 962 m |
| 1040 s | 1030 vs |
| 1130 vs | 1115 w |
| (1270 vw) | 1234 m |
| | 1383$\pm$14 m |
| | 1530 w |
| 1640 m | |
| 3400 v broad | |

However, if ammonia is slowly added to ice-cold thiophosphoryl chloride with vigorous stirring and the mixture then treated with alcohol and cooled in an ice-salt mixture, a precipitate of diammonium monothiophosphate, $(NH_4)_2HPO_3S$, mixed with ammonium chloride, is obtained.[18] The salt is purified by recrystallization. It decomposes on heating, probably forming first diammonium monothiopyrophosphate and then ammonium metaphosphate.[18] The salt may be completely dehydrated over sulphuric acid in a desiccator.[23] The infra-red bands for anhydrous diammonium monothiophosphate are given in Table IV.[23]

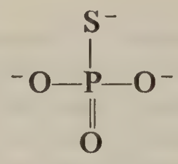
*Table IV.—Infra-red Absorption Frequencies (cm.$^{-1}$) for Anhydrous Diammonium Monothiophosphate*

| cm.$^{-1}$ | | cm.$^{-1}$ | |
|---|---|---|---|
| 450 | w | 1120 | m |
| 475 | w | 1410 | vs |
| 495 | w | 1660 | broad |
| 620 | s | 3150 | v broad |
| 880 | m | 3400 | v broad |
| 1010 | m | | |

Rubidium monothiophosphate, $RbH_2PO_3S$, and cæsium monothiophosphate, $CsH_2PO_3S$ (platelets) are obtained by reaction of the respective chlorides with concentrated aqueous $Na_3PO_3S$ at pH 4.[62]

Attempts have been made to prepare neutral salts of the alkaline-earth metals by precipitation with a solution of a sodium monothiophosphate.[4] Addition of a barium or strontium salt to trisodium monothiophosphate in solution yields the mixed salt $NaBaPO_3S,8H_2O$ or $NaSrPO_3S,8H_2O$, whichever reagent is in excess. A calcium salt gives with trisodium monothiophosphate a slimy precipitate which resembles an orthophosphate. The precipitate appears to be a mixture of hydrated tricalcium monothiophosphate and sodium calcium monothiophosphate octahydrate, $NaCaPO_3S,8H_2O$. The tricalcium salt cannot be separated from this, but if the reaction is carried out by slowly dropping calcium chloride solution into a vigorously stirred solution of trisodium monothiophosphate, rectangular crystals of sodium calcium monothiophosphate octahydrate form in the solution.[4] Refluxing of calcium acetate hemihydrate with diethyl phosphite and sulphur in a mixture of ethyl alcohol and acetic anhydride gave a salt which analysis suggested was monocalcium monothiophosphate, $Ca(H_2PO_3S)_2$.[27]

The heavy-metal monothiophosphates are all unstable, and decompose quickly into the corresponding sulphides. The white precipitate formed when a cadmium salt is added to a solution of a monothiophosphate rapidly turns yellow.[4] The lead salt, which is also white, turns black.[4] Attempts to prepare silver monothiophosphate gave only a black precipitate of silver sulphide,[4,18] In this respect these thiophosphates show some resemblance to the heavy-metal thiosulphates, which decompose to give sulphides and sulphuric acid. Unstable thallium salts, $Tl_3PO_3S$ (pale yellow rhombic crystals) and $TlH_2PO_3S$ (pale brown crystals), have also been prepared by metathesis from $Na_3PO_3S$ and thallium nitrate.[62] When an excess of monothiophosphate ion is added to sodium acetate solution containing Co(II) ions the solution turns deep blue; under the same conditions Ni(II) ions form a greenish-white precipitate, Fe(III) gives a dark brown precipitate, and Mn(II), Al(III) and Zn(II) ions yield white precipitates.[28] The colour of a solution of Cr(III) ions is not affected by monothiophosphate ion, and it has been suggested that this difference might be of some analytical use.[28] On the basis of the products resulting from the reaction of monothiophosphates with alkyl halides, it has been suggested[67] that the ion exists mainly in the mesomeric form



$$^{-}O\text{—}\overset{\displaystyle S^{-}\atop|}{\underset{\|\atop\displaystyle O}{P}}\text{—}O^{-}$$

## Dithiophosphates

Trisodium dithiophosphate (trisodium phosphorodithioate, $Na_3PO_2S_2$) may be prepared from barium tetrathiophosphate, $Ba_3(PS_4)_2,12H_2O$, by treatment with acid.[4] The tetrathiophosphoric acid first formed is immediately hydrolyzed *via* trithiophosphoric acid to dithiophosphoric acid. The acid solution is neutralized with solid sodium hydroxide and a few grams of sodium sulphide are added, together with alcohol. The precipitate formed is dissolved in water and reprecipitated with alcohol to give a product which contains 10% of sodium monothiophosphate. The salt obtained is trisodium dithiophosphate undecahydrate, $Na_3PO_2S_2,11H_2O$, which has an orthorhombic structure, *Pnma* or *Pnz₁a*, with $a = 12{\cdot}51$ A., $b = 13{\cdot}94$ A., $c = 9{\cdot}48$ A., and is isomorphic with the trithiophosphate, $Na_3POS_3,11H_2O$.[16] Anhydrous trisodium dithiophosphate can be obtained by treating the undecahydrate with anhydrous methanol.[62] The $^{31}P$ nuclear magnetic resonance chemical shift for trisodium dithiophosphate in 3% sodium sulphide solution is $-61$ to $-62$ p.p.m., relative to 85% phosphoric acid.[11,14]

Trisodium dithiophosphate reacts with alkyl halides with the elimination of sodium halides, giving alkyl dithiophosphates.[29]

The spots of trisodium dithiophosphate obtained by paper chromatography may be developed with a mixture of sodium fluoresceinate and silver nitrate in aqueous solution giving a green colour, appearing dark under ultra-violet light.[26]

If a suspension of magnesium oxide in ice-cold water is treated with powdered tetraphosphorus decasulphide a precipitate of magnesium dithiophosphate,

$Mg_3(PO_2S_2)_2$, is obtained.[30] By treating this salt with the appropriate base dithiophosphates of sodium, potassium, ammonium, calcium and barium are obtained.[30] Octahedral crystals of triammonium dithiophosphate dihydrate, $(NH_4)_3PO_2S_2,2H_2O$, can be obtained by the action of aqueous ammonia on tetraphosphorus decasulphide at 40°–50°C., or by keeping triammonium trithiophosphate under concentrated aqueous ammonia for 3 days.[62]

Tribarium dithiophosphate, $Ba_3(PO_2S_2)_2$, is said to be formed when barium tetrathiophosphate is dissolved in ice-cooled hydrogen sulphide water.[4] The formation of dithiophosphoric acid, $H_3PO_2S_2$, when sodium acid sulphate is added to the solution, is evidence for the presence of the barium salt.[4]

Zinc dithiophosphate, $Zn_3(PO_2S_2)_2$, has been prepared by treating a solution of phosphorus pentasulphide in ammonia with ammoniacal zinc sulphate solution.[31] It may also be obtained by treating magnesium dithiophosphate with zinc oxide.[30]

Dithiophosphates of thallium and lead have been prepared from magnesium dithiophosphate.[30] Rodlets and needles of $TlH_2PO_2S_2$ can be obtained by using sodium or ammonium dithiophosphate. The manganese, mercury(II), thorium and lanthanum salts decompose fairly rapidly during drying.[30] The salts of bismuth, copper(II), mercury(I), nickel, cobalt, cadmium, silver and iron(II) decompose at once, even when the preparation is carried out in a mixture of alcohol and ice-cold water. Aluminium, zirconium and molybdenum dithiophosphates could not be prepared by this method.[30]

Palladous ions form very insoluble salts with dithiophosphates.[32] These salts are formed in the cold in acid or alkaline solution, and are decomposed only when boiled with mixtures of concentrated acids. These salts have been suggested as a possible means of separating palladium from other heavy metals.[32]

## Trithiophosphates

These are the least known of the thio-orthophosphates. No new method of prepreparing the salts seems to have been devised, and it is difficult to make physical measurements on the acid, which is rapidly hydrolyzed in solution.

*X*-Ray photographs of trisodium trithiophosphate undecahydrate showed it to have the orthorhombic structure, space group *Pnma* or $Pnz_1a$, although the crystals measured were not well formed.[16] The unit cell measurements are $a = 12{\cdot}60$ A., $b = 14{\cdot}02$ A., $c = 9{\cdot}33$ A., very little different from those of trisodium dithiophosphate undecahydrate. Powder photographs confirmed that the two salts are isomorphic.[16]

The $^{31}P$ nuclear magnetic resonance chemical shift for trisodium trithiophosphate in 3% sodium sulphide solution is $-86{\cdot}5$ p.p.m., relative to 85% phosphoric acid.[11,14]

A yellow spot, appearing dark under ultra-violet light, is observed when a paper chromatogram containing sodium trithiophosphate is developed with an aqueous solution of sodium fluoresceinate and silver nitrate.[26]

Triammonium trithiophosphate is obtained by the action of excess of concentrated aqueous ammonia on tetraphosphorus decasulphide at 0°–20°C. It forms fine needles or blunt prisms, which decompose in air and are hydrolyzed by aqueous ammonia to triammonium dithiophosphate. A flocculent yellow precipitate of the thallium salt, $Tl_3POS_3$, is obtained by adding a freshly prepared cold solution of sodium or ammonium trithiophosphate to excess of thallium nitrate solution.[62]

## Tetrathiophosphates

In spite of the instability of the parent acid, several salts of tetrathiophosphoric acid have been prepared and characterized.

Trisodium tetrathiophosphate octahydrate, $Na_3PS_4,8H_2O$, occurs in two crystalline forms, both monoclinic, space groups $P2_1/c$ and $P2_1/a$; the unit-cell constants are $a = 14{\cdot}7$ A., $b = 7{\cdot}09$ A., $c = 14{\cdot}15$ A., $\beta = 92°$, and $a = 13{\cdot}62$ A., $b = 12{\cdot}83$ A., $c = 8{\cdot}69$ A., $\beta = 104°$, respectively.[16] Crystals of the first form were always found to be twinned.[16] The salt is very soluble in water and hydrolyzes in solution, although it is fairly stable in air.[33]

The $^{31}$P nuclear magnetic resonance chemical shift for trisodium tetrathiophosphate in 3% sodium sulphide solution is −87·5 p.p.m.[11,14]

If the appropriate proportions of sodium sulphide, sodium hydrosulphide and tetraphosphorus decasulphide are heated together, an acid salt, disodium tetrathiophosphate, $Na_2HPS_4$, may be obtained.[34] Unless the mixture is heated only up to the point at which it has just fused, the salt decomposes with evolution of hydrogen sulphide. The existence of the salt was confirmed by treatment with absolute alcohol, when no mercaptan was formed; this showed that no free tetraphosphorus decasulphide was present.[34]

A tripotassium salt with behaviour similar to that of the corresponding sodium salt has been prepared by carefully fusing potassium sulphide pentahydrate with tetraphosphorus decasulphide in a porcelain dish.[33] On cooling the filtered solution small tetragonal rods separate. The salt dissolves readily in water with hydrolysis. Like the sodium compound, the salt is fairly stable in air and can be kept in a desiccator over sulphuric acid for many weeks, during which it loses part of its water of crystallization, but appears to be otherwise unchanged.[33] More water is lost on heating at 90°C. A crystal study shows that the salt belongs to the orthorhombic system, with the space group $D_{2h}^{16}$–*Pnma*, with *a*, $9{\cdot}10 \pm 0{\cdot}01$; *b*, $10{\cdot}51 \pm 0{\cdot}01$; and *c*, $9{\cdot}01 \pm 0{\cdot}01$ A., and density 2·13 (calc.).[65]

An ammonium tetrathiophosphate has been prepared by dissolving three times the theoretical amount, relative to ammonium sulphide, of tetraphosphorus decasulphide in a solution of aqueous ammonia saturated with ammonia and hydrogen sulphide.[33] After slow warming the solution is filtered and when kept thick prismatic crystals are formed. These crystals are very stable in air and can be dried without losing ammonia.[33]

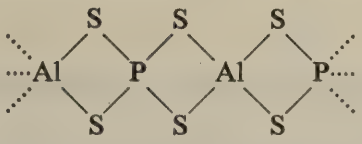
If a suspension of barium hydroxide in water is saturated with hydrogen sulphide, then gently warmed, any residue filtered off, and the cooled solution treated with trisodium tetrathiophosphate, a white curdy precipitate, said to be barium tetrathiophosphate, $Ba_3(PS_4)_2$, is immediately formed.[33] The precipitate, which become voluminous on shaking, is composed of fine microscopic needles which gradually turn yellow in air.

Boron tetrathiophosphate, $BPS_4$, has been prepared by heating boron and phosphorus, boron phosphide, or diboron trisulphide, $B_2S_3$, and phosphorus, with sulphur[35]:

$$\begin{aligned} B+P+4S &= BPS_4 \\ BP+4S &= BPS_4 \\ B_2S_3+2P+5S &= 2BPS_4 \end{aligned}$$

It could not be obtained by heating diboron trisulphide with tetraphosphorus decaoxide. Two modifications were observed, one when the preparation was carried out at 450°–500°C. and the other from a preparation at 650°–700°C. The low-temperature modification forms hygroscopic, colourless, orthorhombic crystals which rapidly decompose in air, giving off hydrogen sulphide. The lattice dimensions are $a = 5{\cdot}60 \pm 0{\cdot}06$ A., $b = 5{\cdot}25 \pm 0{\cdot}06$ A., $c = 9{\cdot}04 \pm 0{\cdot}06$ A., density $d_{20°} = 1{\cdot}98$ g./cm.$^3$ A chain structure has been proposed for these crystals.[35] This modification hydrolyzes to give boron phosphate, and no monothiophosphate could be detected. The high-temperature modification forms brown plates which are more stable in air than those of the low-temperature modification. The lattice dimensions are $a = 10{\cdot}38$ A., $b = 6{\cdot}05$ A., $c = 6{\cdot}69$ A., $\beta = 75°$. The colourless modification is transformed into the brown modification when heated at 650°C. Both modifications decompose on heating *in vacuo* above 750°C., and both explode when heated with air at 1000°C.[35]

Aluminium tetrathiophosphate, $AlPS_4$, could not be prepared by a similar method. It can be obtained as colourless needles and plates, however, when aluminium phosphide is heated at 650°C. in an atmosphere of sulphur.[36] The crystals are hygroscopic and decompose on exposure to air with evolution of hydrogen sulphide. The structure has been shown to be:



with Al–S distance of 2·1 A. in the *a* and *b* directions, P–S distances 2·1 A. in the *a* direction and 2·0 A. in the *b* direction, and Al–P distance 2·8 A.[36]

An *X*-ray study of crystals of copper(II) tetrathiophosphate, $Cu_3PS_4$, shows that they have a structure identical with that of enargite, $Cu_3AsS_4$.[37] The crystals are rhombic, space group $C_{2v}^7$, with two molecules in the unit cell, and contain $PS_4$ tetrahedra. The unit cell parameters are: $a = 6{\cdot}46 \pm 0{\cdot}02$ A., $b = 7{\cdot}43 \pm 0{\cdot}02$ A., $c = 6{\cdot}18 \pm 0{\cdot}2$ A.[37]

A zinc tetrathiophosphate has been prepared by fusion of tetraphosphorus decasulphide and zinc sulphide in an atmosphere of nitrogen at 315°–425°C.[31]

## THIOPHOSPHITES

A substance with a composition corresponding to ammonium monothiophosphite, $(NH_4)_2HPO_2S$, has been detected and isolated by ion-exchange chromatography. It is a white microcrystalline salt, which yields hydrogen sulphide and ammonium phosphite with acid, reduces silver nitrate to metallic silver, and reacts strongly with concentrated nitric acid or bromine water.[64]

It has been reported that hydrates of trisodium trithiophosphite (trisodium phosphorothioite) may be prepared by reaction of lower sulphides of phosphorus with sodium sulphide.[33] Sodium sulphide and tetraphosphorus heptasulphide react rapidly, cooling being necessary. The mixture changes to a thick liquid which is filtered through a warm-water filter and then cooled. On standing the thiophosphite separates in low yield as flat, rectangular, shiny crystals. If tetraphosphorus trisulphide is mixed with sodium sulphide a different hydrate is obtained.[33] The sodium sulphide melts on being warmed, and dissolves the tetraphosphorus trisulphide. A little water is added, and the thick liquid is filtered as before. Fine needles separate on standing; these have substantially the same properties as the product obtained from tetraphosphorus heptasulphide.[33]

The salt is readily soluble in water, apparently decomposing. Hydrogen sulphide is evolved when the solution is acidified, and it rapidly reduces permanganate. The crystals are stable in air.[33] On the basis of a vibration band at 1045 cm.$^{-1}$, said to be due to a P–O vibration, it has been suggested that this supposed thiophosphite salt is a mixture of phosphates.[38]

Ammonium trithiophosphite is reported to be a product of the reaction of tetraphosphorus heptasulphide with liquid ammonia.[39] It is insoluble in liquid ammonia at −33°C., and decomposes slowly in air above −25°C. *In vacuo* it is stable up to 100°C., when mixtures of thiophosphates of varying nitrogen content are formed. At 250°C. the salt decomposes to ammonia, hydrogen sulphide and polymeric PNS. In a stream of ammonia gas at 750°C. polymeric triphosphorus pentanitride, $(P_3N_5)_x$, is formed.

If a concentrated solution of barium sulphide is digested with tetraphosphorus heptasulphide, the solution filtered and a little alcohol added, a precipitate of barium trithiophosphite is formed.[33] This consists of fine, white, microscopic, rhombic prisms. The salt is fairly stable in air and can be kept for some weeks without decomposing. Hydrogen sulphide is evolved on treatment with acid, but even after boiling out all the hydrogen sulphide the solution has strong reducing properties.[33]

Paper-chromatographic studies of the hydrolysis products of tetraphosphorus heptasulphide detected an ion with a P:S ratio of 1:1 and fairly good reducing properties. The colour developed with silver nitrate solution in sulphuric acid

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resembles that developed by phosphite. The ion is probably monothiophosphite, $PO_2S^{3-}$; the $R_f$ value quoted is 0·75, compared with 0·60 for phosphate ion, $PO_4^{3-}$.[38,40]

## OTHER THIO-ACIDS OF PHOSPHORUS

Not many of the lower sulphur-containing acids of phosphorus are known. New ions were detected in the products of hydrolysis of tetraphosphorus heptasulphide.[38] Three unknown compounds with $R_f$ values 0·33 (P:S = 1:2), 0·64 and 0·75 (P:S = 1:1) were observed, the compound with $R_f$ value 0·75 having a lower reducing power than the other two. By analogy with phosphite and hypophosphite ions, the presence of dithiohypophosphite, $H_2PS_2^{2-}$ ($R_f$ value 0·33), monothiohypophosphite, $H_2POS^{2-}$ ($R_f$ value 0·64) and thiophosphite, $HPO_2S^{2-}$ ($R_f$ value 0·75) is suggested.[38]

A compound, $CuPS_2$, is obtained when copper, phosphorus and sulphur, or cupric sulphide and diphosphorus trisulphide, are heated together in a sealed tube under vacuum at 800°C. for 24 hr.[41] It is a yellow, amorphous powder, fairly stable in air, and does not appear to decompose when treated with cold de-aerated water. If heated in a sealed tube under vacuum, it melts over a temperature range of 890°–990°C., but solidifies completely at 910°C. The crystal form is a superstructure of the wurtzite type, with $a = 3·652$ A., $c = 6·085$ A., density 3·55 g./c.c. and P–S distance 2·252 A.[41] At 600°–1000°C. the compound dissociates according to the equation[41]:

$$4CuPS_2 = 2CuPS + Cu_2S + P_2S_5$$

The nature of the bonds between the atoms has not yet been determined.

## THIOPOLYPHOSPHATES

### THIODIPHOSPHATES (THIOPYROPHOSPHATES)

Di-, tri- and tetra-sodium thiodiphosphates have been prepared by reaction of suitable amounts of sodium sulphide and/or hydrosulphide with tetraphosphorus decasulphide[34]:

$$\begin{aligned} 2NaHS + P_2S_5 &= Na_2H_2P_2S_7 \\ NaHS + Na_2S + P_2S_5 &= Na_3HP_2S_7 \\ 2Na_2S + P_2S_5 &= Na_4P_2S_7 \end{aligned}$$

The reactants are ground together and heated until they fuse; if the heating is carried beyond this point hydrogen sulphide is lost from the mixture. Low yields of thiodiphosphate also result from the interaction of disodium phosphite and sulphur in an inert atmosphere.[56]

Hydrogen sulphide is evolved and sulphur deposited when sodium thiodiphosphates are brought into contact with water. Addition of alcohol is accompanied by evolution of a little hydrogen sulphide and acetaldehyde. No mercaptan is formed, showing that the product contains no tetraphosphorus decasulphide and is therefore a definite compound.[34]

Unlike pyrophosphate, ammonium thiodiphosphate gives no precipitate with magnesium, aluminium, manganese, iron, cobalt or nickel salts. Silver salts give a yellow precipitate, which slowly turns red-brown.[56]

### THIOTETRAPHOSPHATES

Hexasodium monothiotetraphosphate, $Na_6P_4O_{12}S$, is prepared by heating a finely-divided mixture of sodium sulphide and sodium metaphosphate in 1 : 4 ratio at 150°C.[42-3] The mixture solidifies to give a dark yellowish-green powder, which dissolves in water to give a milky precipitate of sulphur.[44] A glassy, colourless mass with composition $Na_6P_4O_{10}S_3$ is formed when sodium sulphide is heated to incandescence with tetraphosphorus decaoxide in a ratio of 1 : 2.[42-3] Hexasodium tridecathiotetraphosphate, $Na_6P_4S_{13}$, may be prepared by heating sodium sulphide and tetraphosphorus decasulphide[42-3]

$$3Na_2S + 2P_2S_5 = Na_6P_4S_{13}$$

Compounds with S : O ratios between these extremes may be prepared by fusing the stoicheiometric quantities of sodium tetraphosphate and sulphur or tetraphosphorus decasulphide. These compounds are all extremely soluble in water, and can be used as water-softeners.[42-3]

### OTHER THIOPOLYPHOSPHATES

Oxidation of sodium monothiophosphate with iodine in acid potassium iodide solution[10,59] or manganese dioxide in concentrated hydrochloric acid solution[60] yields a solution of disulphanediphosphonic acid. After neutralization with potassium hydroxide solution, and concentration at 30°C. under a water pump, sodium chloride crystallizes out leaving the salt dipotassium disulphanediphosphonate, $K_2H_2P_2S_2O_6$, in solution. This salt separates on concentration under vacuum in 35% yield, referred to the original weight of trisodium monothiophosphate used. It crystallizes from water as colourless, dense crystals containing no water of crystallization.[10] The salt has a solubility in water of 4·5 g./100 cm.$^3$ $H_2O$; the solution has a pH of *ca.* 5 at 20°C. The two hydrogen atoms may be titrated with alkali using phenolphthalein as indicator. The weakly alkaline solution obtained slowly decomposes to phosphate, hydrogen sulphide and sulphur.[10] Treatment of the salt with perchloric acid gives free disulphanediphosphonic acid.[10,59] Its *X*-ray powder diagram differs from that of the corresponding tetrathionate.[10]

Dipotassium disulphanediphosphonate decomposes when heated to 180°–230°C. yielding potassium metaphosphate and a gas, possibly hydrogen disulphide.[10]

A strongly acid solution of the salt is unaffected by iodine, but weakly acid and pure solutions decolorize iodine. The salt decomposes in the presence of concentrated nitric acid, and sulphur is deposited. A white lead salt is precipitated when lead acetate solution is added to a solution of dipotassium disulphanediphosphonate in water. When warmed this salt decomposes rapidly to lead sulphide. No precipitate is formed with barium chloride solution, but a silver nitrate solution reacts to give black silver sulphide.[10]

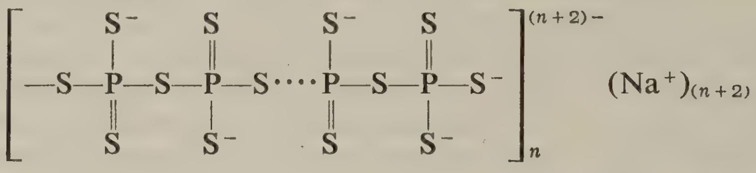
A reddish precipitate is formed when solutions of manganese chloride and dipotassium disulphanediphosphonate are mixed.[10] The precipitate has been assigned the formula $Mn(MnOH)_2P_2S_2O_6,3H_2O$, since three molecules of water are readily lost. More water is lost by heating at 100°C. over phosphorus pentoxide, and some decomposition occurs. The salt always contains some manganous phosphate, formed by hydrolysis during its preparation.[10] A barium salt is obtained from the sodium salt by addition of barium chloride solution at pH 4·5 and 0°C., and a colourless ammonium salt by addition of ammonium chloride followed by methanol. Iodine oxidation of the ammonium salt in acetic acid–ethanol solution gives polymeric $(NH_4PO_2S_2)_x$.[60]

Strontium polyphosphates containing various proportions of sulphur are obtained by dissolving sodium tetrathiophosphate in a strontium hydroxide suspension. On addition of alcohol a white crystalline powder is precipitated.[33]

Monothiophosphoric acid in ethereal solution reacts with sulphur dichloride to give trisulphanediphosphonic acid, $(HO)_2OPS{-}S{-}SPO(OH)_2$, and with sulphur monochloride to give tetrasulphanediphosphonic acid, $(HO)_2OPS{-}S{-}S{-}SPO(OH)_2$, in the form of oily dietherates.[45] The ether may be removed at 0°C. *in vacuo*; the compounds are not stable in air. They decompose in water, but precipitates of the barium salts $Ba_2O_6P_2S_3$ and $Ba_2O_6P_2S_4$, respectively, may be obtained by treating freshly prepared solutions of the acids with a suspension of barium hydroxide. Further polymers in the homologous series $(HO)_2OPS_xPO(OH)_2$ ($x = 1$–$8$) have been obtained by this method.[58]

Tetrathio-orthophosphoric acid reacts with the sulphur chlorides to give light-yellow plastic products which may be represented as $(PS_{5.5})_{2x}$ and $(PS_7)_x$.[45,57] The compounds are stable at room temperature *in vacuo*, are insoluble in organic solvents and water, but are decomposed by alkalis. They decompose on heating at *ca.* 220°C.

Sodium, silver and thallium thiometaphosphates, $(MPS_3)_x$, where $M = Na$, Ag or Tl, are prepared as yellow-brown glasses, by heating tetraphosphorus decaoxide with the appropriate metal sulphide.[46] The sodium thiometaphosphate is extremely hygroscopic. On dissolving in water it releases hydrogen sulphide and forms an acid solution. Addition of barium hydroxide to this solution leads to the formation of a precipitate of tribarium dithio-orthophosphate hexahydrate, $Ba_3(PO_2S_2)_2,6H_2O$. The compound reacts with liquid ammonia at –33°C. to give crystals of composition $NaNH_4(PS_3NH_2)$. The structure was shown to be that of a high molecular-weight polythiophosphate[46]:



$$\left[ -S-\overset{\overset{\large S^-}{|}}{\underset{\underset{\large S}{\|}}{P}}-S-\overset{\overset{\large S}{\|}}{\underset{\underset{\large S^-}{|}}{P}}-S\cdots\overset{\overset{\large S^-}{|}}{\underset{\underset{\large S}{\|}}{P}}-S-\overset{\overset{\large S}{\|}}{\underset{\underset{\large S^-}{|}}{P}}-S^- \right]_n^{(n+2)-} \quad (Na^+)_{(n+2)}$$

The silver and thallium compounds are stable in water and dilute acid, and do not dissolve in organic solvents. This inertness suggests that they are high molecular-weight polymers, almost completely covalently bonded.[46] A compound of trimetaphosphate composition, $Na_3P_3O_8S,6H_2O$, has been obtained by heating sodium hypophosphite with sulphur in a nitrogen atmosphere.[56]

## AMIDOTHIOPHOSPHATES

### THIOPHOSPHORIC TRIAMIDE

Thiophosphoric triamide (phosphorothioic triamide), $PS(NH_2)_3$, may be prepared by refluxing thiophosphoryl trichloride and ammonia in chloroform solution in the presence of ethylamine.[47] It is a colourless, crystalline solid, easily soluble in water. The compound is stable in dry air, but ammonia is evolved on contact with moist air; after a few weeks exposure the end-product is diammonium monothiophosphate, $(NH_4)_2HPO_3S$.

The infra-red absorption bands for solid thiophosphoric triamide are given in Table V.[48]

*Table V.—Infra-red Absorption Frequencies* (*cm.*$^{-1}$) *for Solid Thiophosphoric Triamide in Potassium Bromide*

| | |
|---|---|
| 3330 | 860 |
| 3240 | 715 |
| 1565 | 600 |
| 995, 1010, 1030, 1065 | 460 |
| 895, 930 | |

In aqueous solution, on the other hand, thiophosphoryl chloride and ammonia react exothermically, giving $NH_4(POS(NH_2)_2)$ and $(NH_4)_2(PO_2SNH_2)$.[63]

The $^{31}P$ nuclear magnetic resonance chemical shift for thiophosphoric triamide in dimethyl formamide solution is –59·4 p.p.m., relative to 85% phosphoric acid.[49]

The corresponding hydrazido compound, $PS(N_2H_4)_3$, could not be obtained by treating thiophosphoryl chloride with anhydrous hydrazine; hydrogen sulphide, phosphine and red-yellow polymers were obtained.[50] It has, however, been prepared from thiophosphoryl fluoride and hydrazine under pressure. Its infra-red spectrum has been discussed and partially assigned, the P–S and P–N valence vibrations being qualitatively in accord with the expected values.[69]

Diamidothiophosphoric fluoride, $PS(NH_2)_2F$, is formed when dry ammonia reacts with thiophosphoryl trifluoride, $PSF_3$.[51]

Sodium diamidothiophosphate is formed when the triamide is warmed with dilute sodium hydroxide[47]:

$$PS(NH_2)_3 + NaOH = NaOPS(NH_2)_2 + NH_3$$

Attempts to obtain the free acid were unsuccessful. If this salt is warmed with dilute acid, hydrogen sulphide is evolved. Ammonia is evolved when the compound is heated to 100°C. in a high vacuum and water-soluble compounds are formed. Impure triphosphorus decanitride is obtained as the final product of heating at 800°C. The preparation, and infra-red and Raman spectra of hydrated sodium, calcium, strontium, and barium diamidothiophosphates have been described. The salts can be obtained analytically pure.[66]

Disodium amidothiophosphate, $Na_2PO_2S(NH_2)$, is the product of saponification of diphenyl amidothiophosphate, $(C_6H_5O)_2PSNH_2$.[50] Chromatography shows that the salt is homogeneous. The reaction of hydrazine hydrate with diphenyl chlorothiophosphate, $(C_6H_5O)_2PSCl$, in ethanol yields diphenyl hydrazidothiophosphate, $(C_6H_5O)_2PSN_2H_4$. This compound may be saponified with sodium hydroxide to give disodium hydrazidothiophosphate, $Na_2PO_2SN_2H_4$.[50]

Complex amidothiophosphorus compounds are also obtained from the reaction of tetraphosphorus pentasulphide with liquid ammonia.[52] A canary-yellow hygroscopic solid, said to be $(NH_4)_3[P_4S_5(NH_2)_3]$, is formed when tetraphosphorus pentasulphide is dissolved in liquid ammonia, the solution filtered and evaporated, and the residue kept *in vacuo* for 20 hr. The compound decomposes at room temperature giving off small quantities of ammonia. It is hydrolyzed by moist air and on heating *in vacuo* at 70°C. becomes an intense golden yellow. The product has been assigned the formula $(NH_4)_2[P_4S_5(NH_2)_2]$.[52]

When tetraphosphorus pentasulphide in liquid ammonia is treated with hexamminochromium(III) nitrate a yellow-brown salt which has been given the formula $[Cr(NH_3)_6][P_4S_5(NH_2)_3]$ is formed. The nickel compound, $[Ni(NH_3)_4]_3[P_4S_5NH_2)_3]_2$, is obtained from the liquid ammonia solution of tetraphosphorus pentasulphide and tetramminonickel(I) thiocyanate.[52]

A variety of compounds containing phosphorus, nitrogen and sulphur have also been produced by reaction of tetraphosphorus heptasulphide with liquid ammonia.[39] At $-33$°C. compounds were formed which were assigned the formulæ $(NH_4)_3PS_3$ and $(NH_4)PS_3NH_2$. $(NH_4)_3PS$ is insoluble in liquid ammonia at this temperature, but $(NH_4)_3PS_3NH_2$ remains dissolved at temperatures above $-78$°C. It may also be obtained from phosphorus pentoxide and liquid ammonia at $-78$°C. These compounds are both readily hydrolyzed. $(NH_4)_3PS_3$ decomposes slowly above $-25$°C. and when heated *in vacuo* at 100°C. gives mixtures of different amidothiophosphates.[39] Ammonia, hydrogen sulphide and polymeric $(PNS)_x$ are the final products of heating to 250°C. Polymeric triphosphorus pentanitride is obtained when either $(NH_4)_3PS_3$ or $(NH_4)PS_3NH_2$ is heated in a stream of ammonia at 750°C. At room temperature $(NH_4)PS_3NH_2$ reacts with ammonia in a sealed tube to give $(NH_4)_3PS_3NH$. Tetramminonickel(I) thiocyanate forms the light-blue compound $Ni(NH_3)_6PS_3NH_2$ when treated with $(NH_4)PS_3NH_2$.[39]

Compounds which have been given the formulæ $(NH_4)_3P_3S_3(NH)_3$ and $(NH_4)P_2SN$ are also formed when tetraphosphorus heptasulphide reacts with liquid ammonia. Both are soluble at $-78$°C. Dark-brown, insoluble $[Ni(NH_3)_4][(NH_4)P_3S_3(NH)_3]$ is obtained when $(NH_4)_3P_3S_3(NH)_3$ is treated with tetramminonickel(I) thiocyanate.[39]

The amidoselenophosphate, $(NH_4)[P_4Se_3(NH_2)_2]$, was prepared by reaction of tetraphosphorus triselenide, $P_4Se_3$, with liquid ammonia at $-33$°.[53] At 20°C. this compound decomposes to $(NH_4)_2[P_4Se_3NH]$ which yields $NH_4[P_4Se_3NH_2]$ at 90°C., and finally tetraphosphorus triselenide at 200°C. Tetraphosphorus pentaselenide reacts with gaseous ammonia at 20°C. giving $(NH_4)_2[PSe_3NH_4]$. If the solution remaining after filtration of the product is cooled to $-70$°C. the compounds $(NH_4)_3(PSe_4)$ and $(NH_4)_2[PSe_2(NH_2)NH]$ separate.[53]

## HALOTHIOPHOSPHATES

The hydrolysis of thiophosphoryl trifluoride is believed to occur in stages[54]:

$$PSF_3 \rightarrow HPOSF_2 \rightarrow H_2PO_2SF \rightarrow H_2PO_3S$$

The difluorothiophosphate ion was first isolated as its nitron salt, $[C_{20}H_{16}N_4H^+][PSOF_2^-]$, by the addition of nitron acetate to thiophosphoryl trifluoride.[54] It has since been prepared by the hydrolysis of thiophosphoryl chlorodifluoride[70]; by the interaction of ammonium diamidothiophosphate and hydrogen fluoride[71]; by the reaction of tetraphosphorus hexaoxytetrasulphide and sodium fluoride in acetonitrile[72]; or by the reaction of tetraphenylphosphonium diazidothiophosphate with hydrogen fluoride.[72]

Free difluorothiophosphoric acid is unstable,[54, 73] decomposes on distillation, and slowly hydrolyzes in the cold to monofluorothiophosphate. Sodium, potassium[73] ammonium,[71] quaternary ammonium, phosphonium and arsonium[70, 72–3] salts have been isolated, but no inorganic cations were found to give precipitates in neutral solution.[71] The ammonium salt forms colourless, birefringent, optically negative biaxial leaflets, m.p. 110°, $d_4^{20}$ 1·83 g./c.c. It is very soluble in water and the commoner polar organic solvents, but insoluble in benzene, chloroform and petroleum ether. Nuclear magnetic resonance data have been recorded (see Table VI). The infra-red spectrum shows that this, like other similar anions, has the $O{=}PSX_2$ structure.[70]

Diammonium fluorothiophosphate has been similarly prepared by the action of hydrogen fluoride on a thioamidophosphate. It forms colourless needles, optically positive and biaxial, $d = 1{\cdot}60$ g./c.c., very soluble in water, but insoluble in the commoner organic solvents. The free acid is more stable than $HPSOF_2$, showing no hydrolysis after several hours at room temperature. It is, however, hydrolyzed in boiling water to thiophosphate and phosphate. Aqueous bromine oxidizes the anion to fluorophosphate and phosphate. Lead(II) gives a white precipitate with fluorothiophosphates, and silver(I) a white precipitate which slowly darkens. Other common inorganic cations give no precipitate. The nuclear magnetic resonance spectrum has been recorded (Table VI).[71]

Tetraphenyl-phosphonium or -arsonium chlorofluorothiophosphates have been prepared by the hydrolysis of thiophosphoryl dichlorofluoride in the presence of the appropriate quaternary chloride. However the hydrolysis of thiophosphoryl dibromofluoride gave impure products from which only the difluorothiophosphate could be isolated. These salts as well as the dichlorothiophosphate (*q.v.*) were all soluble in methanol, ethanol or acetone, although with some decomposition.[70]

*Table VI.—Nuclear Magnetic Resonance Data for Halothiophosphates*

| | $^{19}F^{(a)}$ | | $^{31}P^{(b)}$ | | |
|---|---|---|---|---|---|
| Ion | $J_{P-F}$(Hz) | δ(p.p.m.) | $J_{F-P}$(Hz) | δ(p.p.m.) | Ref. |
| $PSOFCl^-$ | 1056 | +43·6 | — | — | 70 |
| $PSOF_2^-$ | — | — | 1120 | −47·1 | 71 |
| | 1097 | +34·1 | 1094 | −46·5 | 73 |
| $PSO_2F^-$ | — | — | 980 | −43·9 | 71 |
| $PS_2F_2^-$ | 1149 | +2·3 | — | −118 | 74 |

(a) Reference to $CCl_3F$.
(b) Reference to 85% $H_3PO_4$.

If water is added to thiophosphoryl trichloride in acetone, dichlorothiophosphoric acid is formed in 99% yield, and can be precipitated as the sparingly soluble nitron salt, $[C_{20}H_{16}N_4H^+][PSOCl_2^-]$[55], or as the tetraphenyl-phosphonium or -arsonium salt.[70] When thiophosphoryl trichloride is titrated with alkali in an acetone–water mixture the steps of the hydrolysis:

$$\mathrm{PSCl_3 \rightarrow HPOSCl_2 \rightarrow H_2PO_2SCl \rightarrow H_3PO_3S}$$

can be demonstrated. Monochlorothiophosphoric acid has a measurable lifetime.[55]

Tetraphosphorus decasulphide reacts with certain metal halides and pseudohalides in media such as water, acetonitrile or 1,2-dimethoxyethane, to give three types of anion:

$$\underset{\mathrm{I}}{[\mathrm{S_2PX_2}^-]}\quad \underset{\mathrm{II}}{[\mathrm{S_2P(X)SP(X)S_2}^{2-}]}\quad \underset{\mathrm{III}}{[\mathrm{S_2P(X)S_2P(X)S_2}^{2-}]}$$

$$(\mathrm{X = F, N_3, CN})$$

The type isolated depends on the salt and solvent used and the isolation procedure. Thus sodium fluoride or azide in water gives primarily compounds of type II, while in acetonitrile type I is mainly formed. Sodium cyanide in acetonitrile gives the anion $[\mathrm{PS_2CN(CSNH_2)}^-]$.[74] Similar treatment of tetraphosphorus hexaoxytetrasulphide gives the anions $[\mathrm{PS_2F_2}^-]$, $[\mathrm{PSOF_2}^-]$, $[\mathrm{PS_2(CN)_2}^-]$ and $[\mathrm{PS_2(N_3)_2}^-]$. $[\mathrm{PSOF_2}^-]$ and $[\mathrm{PSOF(N_3)}^-]$ have been prepared by the action of hydrogen fluoride on $[\mathrm{PS_2(N_3)_2}^-]$.[72]

The dihalodithiophosphates appear to be remarkably stable in acidic or basic solutions. Indeed, the hydronium salts $\mathrm{H_3O^+[PS_2(N_3)_2{}^-]}$ and $\mathrm{H_3O^+[PS_2F_2{}^-]}$ can be distilled *in vacuo* without appreciable decomposition, while the former is stable at room temperature for several months. Cæsium difluorodithiophosphate decomposes at 325 to 375°C., evolving thiophosphoryl fluoride and phosphorus trifluoride. $\mathrm{Pr_4N^+[S_2PCN(CSNH_2)^-]}$ yields mainly hydrogen cyanide, while $\mathrm{Pr_4N^+[PS_2(N_3)_2]}$ evolves nitrogen at about 100°C.[74]

Diamidothiophosphoryl fluoride, $\mathrm{PS(NH_2)_2F}$, has been obtained by reaction of thiophosphoryl trifluoride with dry ammonia gas.[51]

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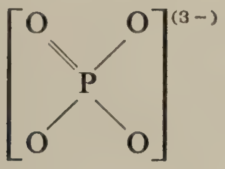
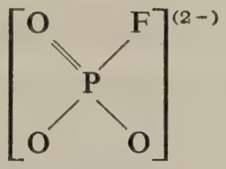
## SECTION XXXI

# FLUOROPHOSPHORIC ACIDS AND THE FLUOROPHOSPHATES

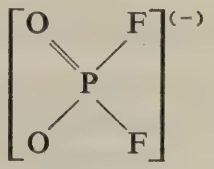
### BY D. A. PALGRAVE

THE fluorophosphates, sometimes called phosphorofluoridates, may be considered as being derived from the orthophosphate ion by replacement of the oxygen atoms by fluorine:

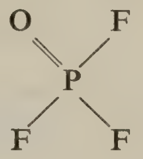


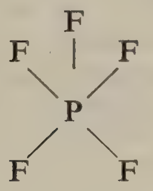


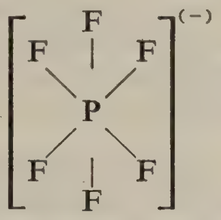
monofluoro-phosphate



difluoro-phosphate



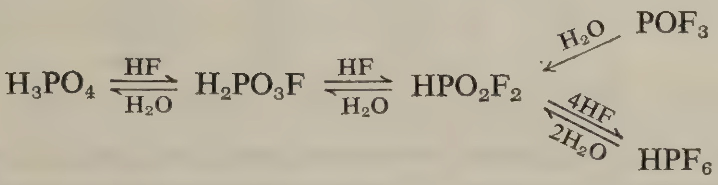




hexafluorophosphate

No fluorophosphates as such have been found in the earth's crust. When fluorine and phosphorus occur together in minerals they usually do so as fluoroapatites, in a lattice containing discrete fluoride and phosphate ions. However Carnot,[1] studying the fluorine content of fossils, suggested that fluorophosphates may take part in the geochemical fluorine cycle. Subsequent investigations[2] of the possible mechanism of fluoroapatite synthesis indicate that in the reaction between calcium pyrophosphate and calcium fluoride, calcium monofluorophosphate may be regarded as an intermediate. Furthermore the presence of randomly distributed $PO_3F^{2-}$ ions would account for the excesses of fluorine and the abnormal densities observed in non-stoicheiometric fluoroapatites. This would also be consistent with the group formula reported[3] for francolite, $[Ca(F,Cl,OH)](Ca,C)_4[(P,C).(O,OH,F)_4]_3$.

Fluorophosphoric acids were first synthesized in 1927 by Lange, who has since contributed very fully toward a general understanding of their chemistry.[4] The following sequence of equilibria has been established[15]:—



$$H_3PO_4 \underset{H_2O}{\overset{HF}{\rightleftharpoons}} H_2PO_3F \underset{H_2O}{\overset{HF}{\rightleftharpoons}} HPO_2F_2 \quad \overset{\xleftarrow{H_2O}\ POF_3}{\underset{\underset{2H_2O}{\overset{4HF}{\rightleftharpoons}}\ HPF_6}{}}$$

and in terms of this a great deal of the behaviour of these acids may be interpreted. The monofluorophosphate ion is quite stable and bears a striking resemblance to the sulphate ion in both physical and chemical properties. The difluorophosphate ion is relatively unstable, and this may account for the dearth of information in the literature. A slight similarity to the perchlorate ion has been suggested.[5] The most stable member of the series is the hexafluorophosphate ion, which in its physical properties has much in common with the chloride ion, and a little in common with the perchlorate ion.

Esters of mono- and di-fluorophosphoric acids have been investigated.[4] Many of the monofluorophosphates are highly toxic materials, being capable of inhibiting the enzyme acetylcholinesterase. This has suggested their possible use as war gases.[52] An account of the chemistry of these compounds may be found in the section dealing with organo-phosphorus derivatives.

## MONOFLUOROPHOSPHORIC ACID

Monofluorophosphoric acid may be formed by the general method of treating a salt with a stronger acid, and this was how an aqueous solution was first obtained[6] although the acid slowly hydrolyzed into orthophosphoric and hydrofluoric acids:

$$Ag_2PO_3F + 2HCl \rightarrow H_2PO_3F + 2AgCl$$

or

$$\underset{\text{(aqueous suspension)}}{Ag_2PO_3F} + \underset{\text{gas}}{H_2S} \rightarrow H_2PO_3F + Ag_2S$$

$$H_2PO_3F + H_2O \rightleftharpoons H_3PO_4 + HF.$$

The last equilibrium has been studied in detail.[8-9] If the mixture is boiled the reaction proceeds quantitatively from left to right. However, at room temperature, provided that the medium is sufficiently acidic, monofluorophosphoric acid can be formed. By applying the law of mass action to the equilibrium, the 'constant'

$$K = \frac{[H_2PO_3F][H_2O]}{[H_3PO_4][HF]}$$

was found to vary with the amount of water added to the reaction mixture of concentrated phosphoric acid and 41% hydrofluoric acid.

*Table I.—Equilibrium Data in the* $H_2O$–$H_3PO_4$–HF–$H_2PO_3F$ *System*

| Initial concentrations (molar) | | | Final concentrations (molar) | | | | |
|---|---|---|---|---|---|---|---|
| $H_2O$ | $H_3PO_4$ | HF | $H_2O$ | $H_3PO_4$ | $H_2PO_3F$ | HF | $K$ |
| 0·279 | 1 | 0·189 | 0·442 | 0·838 | 0·162 | 0·027 | 3·17 |
| 1·015 | 1 | 0·189 | 1·129 | 0·887 | 0·113 | 0·076 | 1·89 |
| 1·642 | 1 | 0·190 | 1·712 | 0·930 | 0·070 | 0·120 | 1·07 |
| 1·928 | 1 | 0·191 | 1·985 | 0·943 | 0·057 | 0·134 | 0·90 |
| 2·442 | 1 | 0·190 | 2·478 | 0·965 | 0·035 | 0·154 | 0·59 |
| 3·039 | 1 | 0·188 | 2·991 | 0·976 | 0·024 | 0·160 | 0·45 |
| 3·507 | 1 | 0·191 | 3·527 | 0·980 | 0·020 | 0·171 | 0·41 |
| 3·900 | 1 | 0·192 | 3·196 | 0·983 | 0·017 | 0·175 | 0·38 |
| 3·957 | 1 | 0·188 | 3·970 | 0·987 | 0·013 | 0·174 | 0·31 |
| 6·608 | 1 | 0·186 | 6·617 | 0·991 | 0·009 | 0·176 | 0·35 |
| 13·939 | 1 | 0·182 | 13·943 | 0·996 | 0·004 | 0·178 | 0·31 |

From the results in Table I it can be seen that as the proportion of water added to the mixture is increased, the value of $K$ gradually assumes a constant level. When only a small quantity of water is present large yields of monofluorophosphoric acid are obtained. A more complex process than that represented by the equation above seems to be taking place. No simple satisfactory explanation has been advanced and it has recently been suggested[11,16] that the problem could best be resolved using modern physical techniques. By increasing the concentration of both hydrofluoric acid and water the value of $K$ reaches 3·47, then levels off in the region of 0·8–0·9. Thus, if concentrated phosphoric acid is mixed with about 3·5 times its weight of 41% hydrofluoric acid, one-third of the phosphate is converted to fluorophosphate. Monopotassium phosphate can be fluorinated to the same extent by adding a large excess of aqueous hydrofluoric acid ($K = 0{\cdot}71$). The presence in the mixture of a 'strong' acid, e.g. perchloric acid, can increase the value of $K$ to 23·7.

The reaction between anhydrous phosphoric and hydrofluoric acids yields mainly monofluorophosphoric acid, but the formation of other fluorophosphoric acids is possible.

If phosphorus pentoxide is dissolved in 40% hydrofluoric acid solution several products are formed, the final mixture consisting of an aqueous solution of monofluorophosphoric, orthophosphoric and hydrofluoric acids. High yields of monofluorophosphoric acid can be obtained by arranging for the value of $x$ in the following equation to be zero:

$$P_2O_5 + (2-x)HF + (1-x)H_2O \rightarrow xHPO_2F_2 + (2-x)H_2PO_3F$$

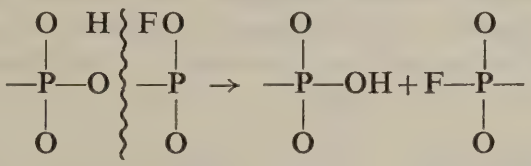
This is brought about by the use of 69% hydrofluoric acid,[12] and a reaction temperature of 150°C. The maximum value of $x$ is unity, when a stoicheiometric mixture of mono- and di-fluorophosphoric acids, is obtained. These can be separated by vacuum distillation.[13]

The reaction:

$$HPO_3 + HF \rightarrow H_2PO_3F$$

has been observed to proceed to completion,[7,14] albeit slowly owing to the viscous nature of the metaphosphoric acid.

The mechanism of the two reactions suitable for the preparation of monofluorophosphoric acid is still obscure,[4] although it seems likely that in each case hydrofluorolysis of P–O–P bridges is a fundamental step:



$$-\overset{O}{\underset{O}{P}}-\overset{H}{O}\,\Big\}\,\overset{F}{}-\overset{O}{\underset{O}{P}} \rightarrow -\overset{O}{\underset{O}{P}}-OH + F-\overset{O}{\underset{O}{P}}-$$

Such a process would explain why orthophosphoric acid comes to be detected in the final products.

Monofluorophosphoric acid is also produced by the hydrolysis of phosphoryl trifluoride.[5]

## Physical Properties

At room temperature monofluorophosphoric acid is a colourless oily liquid ($d_4^{25}$ 1·818) similar to sulphuric acid in appearance.[15] When cooled the acid becomes very viscous at −20°C., eventually setting rigid at −70°C. without signs of crystallization.[7]

Nuclear magnetic resonance spectra have been examined by several workers,[16–18] and provide evidence of a tetrahedral configuration for the $PO_3F^{2-}$ ion, with one of the oxygen atoms of the orthophosphate ion replaced by fluorine, as expected from general stereochemical considerations.

The fluorine resonance in monofluorophosphoric acid is shown in Table II but the phosphorus resonance is obscured by other phosphorus compounds present.[17]

*Table II.—Nuclear Magnetic Resonance Spectrum of Monofluorophosphoric Acid*

| Resonance | Line structure | Applied field (gauss) | Splitting (gauss) | Chemical shift* |
|---|---|---|---|---|
| Fluorine | (1–1) | 6365 | 0·238 | $-0{\cdot}25\times10^{-5}$ |
| | | 4180 | 0·241 | |
| | | 170 | $0{\cdot}240\pm0{\cdot}001$ | |

* Referred to trifluoroacetic acid.

## Chemical Properties

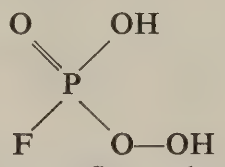
The anhydrous acid can be heated to 185°C. under reduced pressure with only slight decomposition.[7] Provided that no moisture is present glass is not attacked, but the ease of hydrolysis, at low pH values, to orthophosphoric acid and hydrofluoric acid makes glass unsuitable for use either as a storage or a reaction vessel under aqueous conditions.

Aqueous monofluorophosphoric acid behaves as a dibasic acid, although one hydrogen is much more readily ionized than the other. The titration curve[19] is very similar to that of orthophosphoric acid, the two neutral points occurring at pH 3·5 and 8·5 respectively, corresponding to the first and second ionization constants of 0·28 and $1{\cdot}58\times10^{-5}$. Conductance measurements suggest that the difference between the ionization constants is greater, and even that the acid may be monobasic. This behaviour is attributed to the formation of intramolecular hydrogen bonds, –F····H–O–. The equivalent conductance is 413·8 $\text{ohm}^{-1}$ $\text{equiv.}^{-1}$ $\text{cm.}^{-1}$ [130]

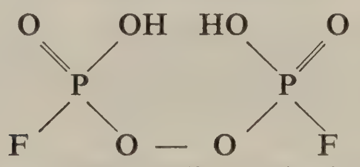
The anhydrous acid and very concentrated aqueous solutions attack most common metals and their alloys, including stainless steel. However silver, platinum and aluminium are not affected; neither are polyethylene, polystyrene and polymeric fluorocarbons. Rubbers, apart from butyl rubber, are not suitable for handling the concentrated acid, although dilute solutions have little or no effect on them. The dilute acid attacks aluminium and titanium[96]; the coating produced on the latter metal facilitates subsequent cold deformation operations. Aqueous solutions of the acid are readily absorbed by cellulose, generating extensive swelling.[15]

Monofluorophosphates may readily be prepared from aqueous solutions of the acid.[7]

Electrolytic oxidation results[28] in the formation of mono- and di-peroxyfluorophosphoric acids in yields of up to 2%:



monoperoxymonofluorophosphoric acid



diperoxydifluorodiphosphoric acid

Monofluorophosphoric acid has been mentioned in several patents describing various organic operations. It can function catalytically when olefines are polymerized,[21] *iso*paraffins are alkylated,[22] and when oils are refined[12] under non-oxidizing conditions. Various derivatives of monofluorophosphoric acid have been utilized as alkylation catalysts, including an addition compound with boron trifluoride $H_2PO_3,BF_3$ [94] and compounds from aluminium chloride[95] in which one or more of the chlorine atoms are replaced by acid monofluorophosphate groups, e.g. $AlCl_2(HPO_3F)$, $AlCl(HPO_3F)_2$. A further group of patents describes applications depending on the reactions of the acid with siliceous matter, e.g. the removal of residual sand from metals cast in sand moulds,[23] the improvement of permeability in certain geological operations[24-5,101-2] and the improvement of the physical properties of asphalt by blowing with air saturated with monofluorophosphoric acid,[26] or alternatively by heating the asphalt with the acid and subsequently blowing with air.[100] Metal cleaning and fungicidal properties have also been suggested.[15]

## MONOFLUOROPHOSPHATES

Monofluorophosphates were first obtained by Lange[5] by fusion of phosphorus pentoxide with ammonium fluoride:

$$P_2O_5 + 3NH_4F \rightarrow NH_4PO_2F_2 + (NH_4)_2PO_3F$$

At the reaction temperature (*ca.* 135°C.) the monofluorophosphate loses ammonia:

$$(NH_4)_2PO_3F \rightarrow NH_3 + NH_4HPO_3F$$

and consequently the alcoholic extract from the fusion mixture is treated with ammoniacal alcohol until the solution is neutral, when diammonium monofluorophosphate is precipitated. These reactions have been discussed.[27-30] The mechanism of the fusion reaction would seem to resemble the hydrofluorolysis postulated to explain the reaction between hydrofluoric acid and phosphorus pentoxide, which gives rise to monofluorophosphoric acid.

Monofluorophosphates are prepared by the neutralization of the acid by a base, e.g.[7]:

$$PbO + H_2PO_3F \rightarrow PbPO_3F + H_2O$$

or by a suitable double decomposition technique. The choice of method depends on the solubility of the desired salt. Since the solubilities of monofluorophosphates are very similar to those of the corresponding sulphates it is possible to select a suitable reaction fairly easily; e.g.:

$$CaCl_2 + Na_2PO_3F + 2H_2O \rightarrow CaPO_3F.2H_2O\downarrow + 2NaCl^{31}$$
$$2KOH + (NH_4)_2PO_3F \rightarrow K_2PO_3F + 2NH_3 + 2H_2O^{27-8}$$
$$Ag_2PO_3F + 2NaCl \rightarrow Na_2PO_3F + 2AgCl^{6,111}$$

If the sulphate is sparingly soluble the monofluorophosphate can be filtered off. If the sulphate is soluble then the use of either the ammonium salt or the silver salt is advisable, since ammonia can be removed from an aqueous solution by blowing air through it, whilst the silver chloride is readily removed by filtration. To obtain solid monofluorophosphates the solutions are evaporated to dryness *in vacuo* at room temperature.

The foregoing are illustrations of general methods of preparing salts. However one method, the hydrolysis of difluorophosphates, is less general:—

$$KPO_2F_2 + 2KOH \rightarrow K_2PO_3F + KF + H_2O^{6}$$

Perhaps the most useful technique is that of Hill and Audrieth[32-3] in which an anhydrous alkali-metal metaphosphate is fused with an alkali-metal fluoride and then quenched:

$$Na_3P_3O_9 + 3NaF \rightarrow 3Na_2PO_3F$$
$$(KPO_3)_n + nKF \rightarrow nK_2PO_3F$$

The phase diagram for mixtures of potassium metaphosphate and potassium fluoride is given in Fig. 1. The crystallization surface of the $K^+,Na^+ \| F^-,PO_3^-$ ternary reciprocal system has also been studied. Only sodium and potassium monofluorophosphates, and their double salts with the corresponding fluorides, were observed.[131] Traces of pyrophosphates or other condensed phosphates may be eliminated by treating an aqueous solution of the alkali metal monofluorophosphate with silver monofluorophosphate. It seems likely that the mechanism is analogous to that of the reaction between metaphosphoric acid and hydrogen fluoride. Hill[34] has suggested that metaphosphates in such high temperature systems can be regarded as Lewis acids, capable of reacting with an electron donor such as the fluoride ion.

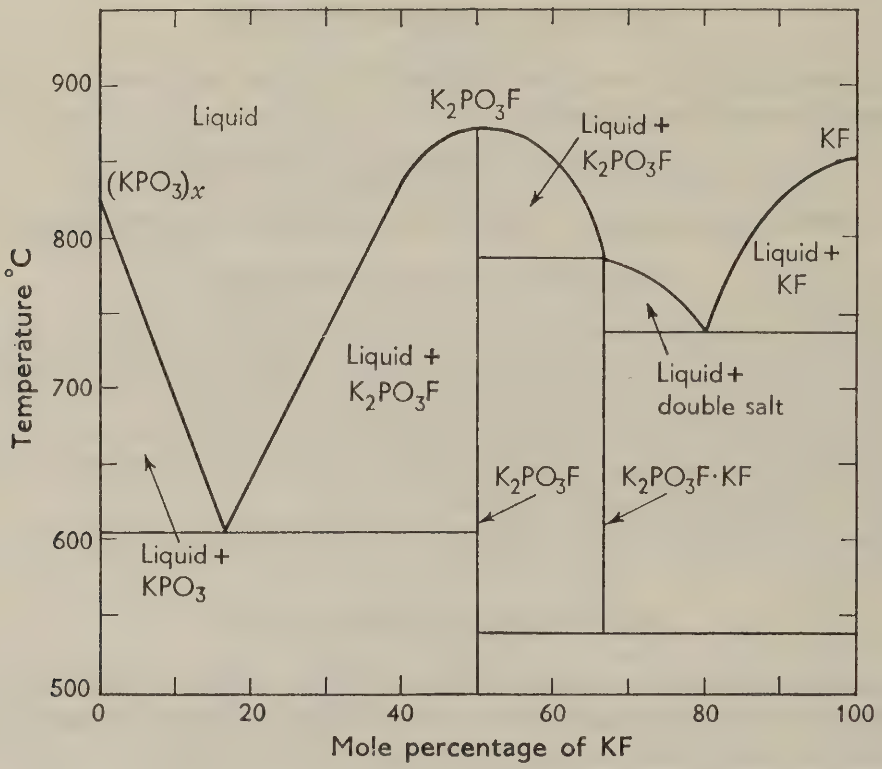


FIG. 1—The potassium metaphosphate–potassium fluoride system

Other studies of the interaction between fluorides and polyphosphates of various kinds have been made.[132-5] Although only monofluorophosphates have been detected, there is evidence for P–F compounds of other kinds, possibly polyphosphate in character.

## Physical Properties

Many workers have drawn attention to the remarkable crystallographic similarity between the monofluorophosphates and the sulphates.[35-41] This is undoubtedly due to the isosteric and isoelectronic nature of the two ions. Several examples of isomorphism have been reported by these investigators. $CuPO_3F,5H_2O$, $CoPO_3F,6H_2O$ and $NiPO_3F,7H_2O$ are isomorphous with $CuSO_4,5H_2O$, $CoSO_4,6H_2O$ and $NiSO_4,7H_2O$, respectively.[36] Similarly in another study $NiPO_3F,6H_2O$, $3CdPO_3F,8H_2O$, $CdPO_3F,H_2O$, $MnPO_3F,2H_2O$, $MnPO_3F,H_2O$, $Cr_2(PO_3F)_3,18H_2O$, $Cr_2(PO_3F)_3,15H_2O$ and $Cr_2(PO_3F)_3,6H_2O$ where shown to be stable at 50°. Each of these (except the dihydrated manganese salt) has an equivalent sulphate hydrate.[136] Magnetic susceptibility measurements have been recorded for these latter salts.[137] Many double salts of the alum and schoenite type have been prepared. Some are mixed monofluorophosphates and others mixed monofluorophosphate-sulphates[36,40]

| | |
|---|---|
| $NiPO_3F,(NH_4)_2PO_3F,6H_2O$; | $CoPO_3F,(NH_4)_2PO_3F,6H_2O$; |
| $(NH_4)_2PO_3F,Al_2(PO_3F)_2,24H_2O$; | $NiSO_4,(NH_4)_2PO_3F,6H_2O$; |
| $CuSO_4,(NH_4)_2PO_3F,6H_2O$; | $CoSO_4,(NH_4)_2PO_3F,6H_2O$; |
| $ZnSO_4,(NH_4)_2PO_3F,6H_2O$; | $MnSO_4,(NH_4)_2PO_3F,6H_2O$; |
| $MgSO_4,(NH_4)_2PO_3F,6H_2O$; | $(NH_4)_2PO_3F,Al_2(SO_4)_3,24H_2O$. |

The sulphate and monofluorophosphate of potassium are so similar that mixed crystals are formed in all proportions.[36] Calcium monofluorophosphate, like calcium sulphate, forms a monoclinic dihydrate which decomposes to a hemihydrate on heating.[31]

This similarity to the sulphates extends to the solubilities in water, the salts of the alkali metals being readily soluble and those of the alkaline earths being only sparingly soluble.[6] Some values are given in Table III and shown graphically in Fig. 2.

*Table III.—Solubilities of Monofluorophosphates and Sulphates in Water at* 20°C. (expressed in moles/litre)

| Cation | Monofluorophosphates | Sulphates |
|---|---|---|
| Calcium | $6{\cdot}3\times10^{-2}$ | $1{\cdot}5\times10^{-2}$ |
| Strontium | $5{\cdot}5\times10^{-2}$ | $6\times10^{-4}$ |
| Barium | $6\times10^{-4}$ | $1\times10^{-5}$ |
| Silver | $5{\cdot}93\times10^{-2}$ | $2{\cdot}51\times10^{-2}$ |
| Lead | $3{\cdot}2\times10^{-4}$ | $1{\cdot}3\times10^{-4}$ |
| Mercury | $5\times10^{-4}$ | $8\times10^{-4}$ |

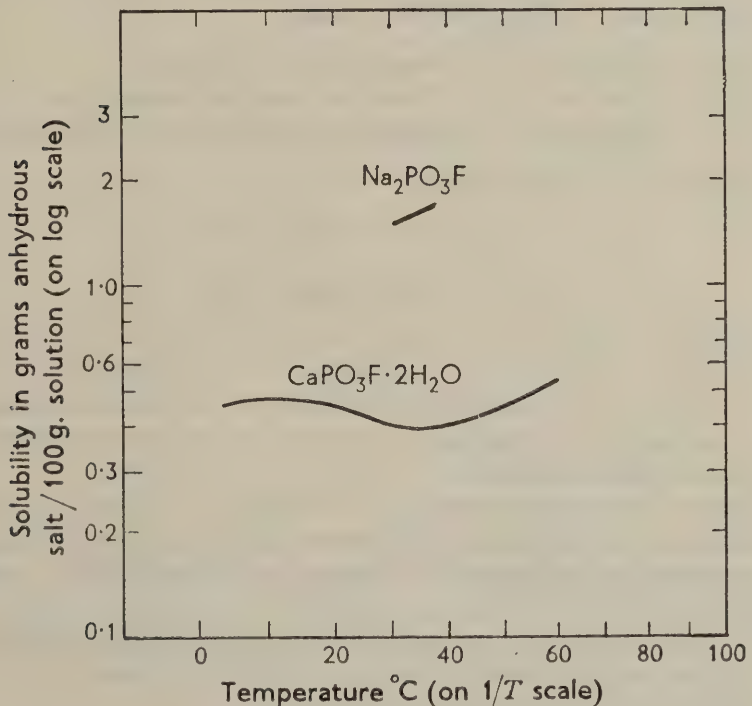


FIG. 2.—Solubilities of sodium and calcium monofluorophosphates

A subsequent determination of the solubility of barium monofluorophosphate gave a value of $7{\cdot}7\pm0{\cdot}6\times10^{-4}$ moles/l. The mean activity coefficient of barium monofluorophosphate as a function of ionic strength was found to approach the limiting Debye–Hückel slope for a 2:1 electrolyte.[138]

**Refs. p. 868**

*X*-Ray diffraction studies[42-3] provide further evidence of sulphate–monofluorophosphate isomorphism. The powder diagrams of $BaSO_4$ and $BaPO_3F$[42] are almost identical, as are those of $K_2SO_4$ and $K_2PO_3F$.[43] Barium monofluorophosphate usually crystallizes in the orthorhombic system, with unit cell dimensions *a* 8·68, *b* 5·63, *c* 7·28 A. and *V* 356 $A^3$., although the compound may assume a more stable monoclinic form. Lead fluorophosphate, $PbPO_3F$, also appears to have an orthorhombic lattice, with $a = 6{\cdot}951$, $b = 8{\cdot}521$, $c = 5{\cdot}470$ A., $d_{obs.} = 6{\cdot}15$, $d_{calc.} = 6{\cdot}24$ g./c.c. It is probably isostructural with lead sulphate and barium sulphate, *H*2 type.[139] Single crystal studies of the potassium salts indicate that both are orthorhombic (space group *Pnam* $D_{2h}^{16}$). Each ion is tetrahedral although the $PO_3F^{2-}$ ion is slightly distorted.

Bond distances (A.) are given below:

| | | | |
|---|---|---|---|
| $S{-}O_1$ | $1{\cdot}54 \pm 0{\cdot}06$ | $P{-}F_1$ | $1{\cdot}55 \pm 0{\cdot}08$ |
| $S{-}O_2$ | $1{\cdot}51 \pm 0{\cdot}16$ | $P{-}O_2$ | $1{\cdot}44 \pm 0{\cdot}16$ |
| $S{-}O_3$ | $1{\cdot}47 \pm 0{\cdot}12$ | $P{-}O_3$ | $1{\cdot}53 \pm 0{\cdot}10$ |
| Mean | $1{\cdot}52 \pm 0{\cdot}02$ | Mean | $1{\cdot}52 \pm 0{\cdot}04$ |

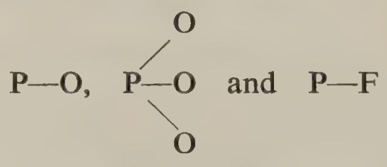
Bond angles (°) are as follow:

| | | | |
|---|---|---|---|
| $O_1{-}S{-}O_2$ | $112 \pm 8$ | $F_1{-}P{-}O_2$ | $115 \pm 8$ |
| $O_1{-}S{-}O_3$ | $107 \pm 4$ | $F_1{-}P{-}O_3$ | $96 \pm 5$ |
| $O_2{-}S{-}O_3$ | $110 \pm 8$ | $O_2{-}P{-}O_3$ | $119 \pm 8$ |
| $O_3{-}S{-}O_3$ | $111 \pm 5$ | $O_3{-}P{-}O_3$ | $109 \pm 7$ |
| Mean | $109 \pm 2$ | Mean | $106 \pm 9$ |

The infra-red spectra of a large number of monofluorophosphates have been examined[44-5, 97] including $(NH_4)_2PO_3F,H_2O$; $Li_2PO_3F,3H_2O$; $Na_2PO_3F$; $K_2PO_3F$; $CaPO_3F,xH_2O$; $SrPO_3F,xH_2O$; $BaPO_3F$; $PbPO_3F$; $Ag_2PO_3F$. The principal absorption regions occur in the following ranges:

| | |
|---|---|
| 1210 – 1120 cm.$^{-1}$ | Very strong broad peak |
| 1022 – 990 cm.$^{-1}$ | Strong or medium absorption |
| 832 – 721 cm.$^{-1}$ | Broad absorption often two peaks |

These regions probably correspond to



$$P{-}O,\quad P\!\begin{smallmatrix}\diagup O\\ {-}O\\ \diagdown O\end{smallmatrix}\quad \text{and}\quad P{-}F$$

groupings respectively. The position of the absorption bands associated with P–O stretching is anomalous. This anomaly is thought to be correlated with the electronegative character of the fluorine.

Nuclear magnetic resonance spectra of aqueous solutions of sodium monofluorophosphate have been obtained.[17] With an applied field of 6365 gauss a fluorine doublet was observed, of splitting 0·195 gauss, and chemical shift, with respect to trifluoracetic acid, $+2{\cdot}68 \times 10^{-5}$.

Conductivity measurements[46] indicate that the sodium salt behaves as a strong electrolyte with equivalent conductance $\Lambda_0 = 113{\cdot}5 \pm 0{\cdot}5$ ohm$^{-1}$ (at 25°C.). The ionic conductance of the $PO_3F^{2-}$ ion is 63·3 ohm$^{-1}$.

The density of aqueous solutions of sodium monofluorophosphate has been measured at 25°C. over the concentration range 0·4 to 2·0 M. The partial molal volume is a linear function of the square root of the molality.[140] The fluidity (reciprocal viscosity), $\phi$, of such solutions at the same temperature is given by:

$$\phi = 1 - 0{\cdot}01568c^{1/2} - 0{\cdot}4160c$$

over the concentration range 0·014 to 0·5 M.[141]

## Chemical Properties

Aqueous solutions of the monofluorophosphates of the alkali metals are alkaline to methyl orange and neutral to phenolphthalein. Provided that cations capable of forming less soluble phosphates or fluorides are absent, a neutral or weakly alkaline solution is exceedingly stable, even when boiled, whilst a 1% solution at 95°C. is hydrolyzed less than 1% per hour.[15] The hydrolysis reaction appears to be of first order[19,112] in monofluorophosphate concentration. The thermodynamic dissociation constant of $HPO_3F^-$ is $0{\cdot}76 \times 10^{-5}$ at 25°C.[113] The considerably greater acidity of $HPO_3F^-$ (compared with that of $H_2PO_4^-$) has been shown to be due mainly to the respective enthalpies of dissociation. The alkaline hydrolysis of monofluorophosphate, which has been studied in the temperature range 120°–140°C.,[114] appears to take place by two parallel processes, the velocities $v_1$ and $v_2$ being given by $v_1 = k_1[PO_3F^{--}]$, $v_2 = k_2[PO_3F^{--}][OH^-]$. However, in strongly alkaline or acidic conditions rapid hydrolysis takes place[4] as shown in Fig. 3.

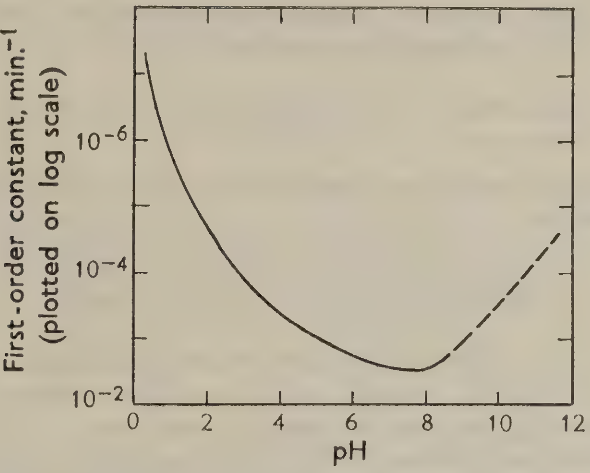


Fig. 3.—Hydrolysis of monofluorophosphate at 80°C

$$K_2PO_3F + H_2O \rightarrow KH_2PO_4 + KF$$

The activation energy for this hydrolysis is 8 kcal./mole.[19,111]

Hydrolysis of a saturated solution of the dihydrate of the calcium salt[115] results in the comparatively slow formation of calcium fluoride and monocalcium phosphate at room temperature:

$$2CaPO_3F{,}2H_2O \rightarrow CaF_2 + Ca(H_2PO_4)_2 + 2H_2O$$

At temperatures somewhat above 50°C. the decomposition is much more rapid and the two products of the reaction combine in the presence of water to give fluorapatite, whilst at still higher temperatures pyrophosphates are formed as discussed below.

Sodium, potassium and ammonium monofluorophosphates have been electrolyzed in aqueous solution[28,47] giving rise to mono-and di-peroxyfluorophosphoric acids which have not been isolated, although thay have been identified by studying the variation in alkalinity of the electrolyte. The potassium salt gives the greatest yields, which can be enhanced by the addition of fluorides. If the pH of the electrolyzed solutions is allowed to rise the peroxy-acids decompose, the first reverting to a monofluorophosphate and the other hydrolyzing to a peroxyphosphate.

The action of heat on monofluorophosphates in the solid state invariably brings about decomposition,[34] especially if moisture is present in the atmosphere, when hydrolysis occurs as discussed above. Thus thermogravimetric analysis of calcium monofluorophosphate dihydrate indicates that it eventually decomposes to calcium pyrophosphate, hydrogen fluoride and water[48]:

$$\mathrm{CaPO_3F,2H_2O} \xrightarrow{100°\mathrm{C}} \underset{\text{phase}}{\text{amorphous}} \xrightarrow{400°\mathrm{C}} \alpha\text{-}\mathrm{Ca_2P_2O_7} \xrightarrow{550°\mathrm{C}} \beta\text{-}\mathrm{Ca_2P_2O_7}$$

When the corresponding strontium compound is heated[116–7] it decomposes eventually forming strontium pyrophosphate, strontium fluorapatite, and phosphoryl trifluoride:

$$\mathrm{5SrPO_3F,H_2O} \xrightarrow{90\text{–}150°\mathrm{C}} \mathrm{5SrPO_3F} \xrightarrow{460°\mathrm{C}} \mathrm{2Sr_2P_2O_7 + SrF_2 + POF_3}$$

$$\mathrm{18Sr_2P_2O_7 + 14SrF_2} \xrightarrow{800°\mathrm{C}} \mathrm{5Sr_{10}(PO_4)_6F_2 + 6POF_3}$$

Any moisture present brings about the evolution of hydrogen fluoride:

$$\mathrm{2SrPO_3F + H_2O \rightarrow Sr_2P_2O_7 + 2HF}$$

Similar analyses of the potassium salt revealed transition points at 443°C. and 800°C.[49] The following sequence was suggested:

$$\underset{\text{orthorhombic}}{\beta\text{-}\mathrm{K_2PO_3F}} \xrightarrow{443°\mathrm{C}} \underset{\text{hexagonal}}{\mathrm{K_2PO_3F}} \xrightarrow{800°\mathrm{C}} \alpha\text{-}\mathrm{K_2PO_3F}$$

although a subsequent investigator[43] pointed out that the following reactions would explain the observations:

$$\mathrm{5K_2PO_3F \rightarrow 2K_4P_2O_7 + 2KF + POF_3}$$
$$\mathrm{2K_2PO_3F + H_2O \rightarrow K_4P_2O_7 + 2HF}$$

The view that phosphoryl trifluoride may be produced is supported by evidence from the reaction between calcium fluoride and phosphorus pentoxide,[50] where a slight trace was detected among the gaseous reaction products.

Sodium fluorophosphate melts at 625°C., and has been reported to decompose at higher temperatures in the presence of moisture yielding pyrophosphate and hydrogen fluoride.[34] Furthermore the molten salt is very reactive towards metal surfaces,[15] a property which renders it suitable as a flux. The main application of sodium monofluorophosphate is however in the prevention of dental caries, where it has been shown to act by diminishing the rate of solution of tooth enamel.[53, 142]

Ammonium monofluorophosphate monohydrate loses its water of crystallization at 105°C., and further heating causes the loss of one molecule of ammonia giving an acid salt, $\mathrm{NH_4HPO_3F}$, which melts at 225·5°C. without further decomposition. If the monohydrate is exposed to the atmosphere it tends to effloresce.

Mono-amidophosphates have been prepared[51] from alkali metal monofluorophosphates. Under alkaline conditions, at pressures between 5 and 20 atm. and at temperatures between 90° and 100°C., ammonia reacts with sodium monofluorophosphate to yield $\mathrm{NaHPO_3NH_2,\frac{1}{2}H_2O}$.

It has been suggested,[11] on the basis of data obtained from a study of the $\mathrm{(KPO_3)_n}$–KF system (Fig. 1), that a double salt between potassium monofluorophosphate and potassium fluoride is formed (see also Ref. 131 and page 848).

## DIFLUOROPHOSPHORIC ACID

Difluorophosphoric acid was first recognized in the dilute aqueous solution obtained by the action of dilute nitric acid on a cold saturated solution of the nitron salt,[5] but was not isolated because of hydrolysis. Although the acid appears in the general sequence of equilibria which relate to the fluorophosphoric acids:

$$\mathrm{H_3PO_4} \underset{\mathrm{H_2O}}{\overset{\mathrm{HF}}{\rightleftharpoons}} \mathrm{H_2PO_3F} \underset{\mathrm{H_2O}}{\overset{\mathrm{HF}}{\rightleftharpoons}} \mathrm{HPO_2F_2} \underset{\mathrm{2H_2O}}{\overset{\mathrm{4HF}}{\rightleftharpoons}} \mathrm{HPF_6}$$

these reactions do not afford a convenient basis of preparation. However, like monofluorophosphoric acid, difluorophosphoric acid can arise from the interaction of phosphorus pentoxide and hydrofluoric acid[12]:

$$P_2O_5+(2+x)HF+(1-x)H_2O \rightarrow xHPO_2F_2+(2-x)H_2PO_3F$$

Yields are greatest when $x$ is unity, i.e. when anhydrous hydrofluoric acid is used. The two acids can be separated by vacuum distillation. Fluorosulphonic acid has been used as a catalyst for the reaction.[143]

A novel method of preparation consists in causing monofluorophosphoric acid to react with phosphoryl trifluoride,[54] since no water or hydrogen fluoride is present to lead to the formation of other fluorophosphoric acids:

$$\underset{\text{anhydrous}}{H_2PO_3F}+\underset{\text{gaseous}}{POF_3} \rightarrow 2HPO_2F_2$$

Pure difluorophosphoric acid can be obtained in high yield by distilling the liquid product under reduced pressure. The anhydrous acid has also been obtained[50] from the reaction between calcium fluoride and phosphorus pentoxide. Here it probably arises by hydrolysis of phosphoryl trifluoride, the major product of the reaction, brought about by traces of water present in the reagents.

## Physical Properties

The anhydrous acid is a clear mobile liquid at ordinary temperatures. On exposure to a damp atmosphere dense irritant fumes form. Vapour pressure measurements in the temperature range 50°–90°C. have been published.[54] Below are experimental and calculated data (Table IV) obtained by substituting in the equation:

$$\log_{10}p\ (\text{mm.}) = -\frac{1732{\cdot}2}{T}+7{\cdot}333$$

*Table IV.—Vapour Pressure of Difluorophosphoric Acid*

| $T$ (°K.) | $p_{\text{mm.}}$(observed) | $p_{\text{mm.}}$(calculated) |
|---|---|---|
| 324·8 | 100·5 | 100·4 |
| 335·4 | 147·7 | 148·0 |
| 344·3 | 201·4 | 201·2 |
| 351·0 | 251·4 | 251·0 |
| 356·8 | 301·4 | 301·9 |
| 366·0 | 399·9 | 399·7 |

Other authors have given the vapour pressure equation:

$$\log_{10}p\ (\text{mm.}) = -\frac{421{\cdot}195}{T}-0{\cdot}478214\log T+0{\cdot}0137121T$$

covering the range −22° to 108°C.[143] Because the acid tends to decompose on distillation the boiling point at 760 mm. has been obtained by extrapolation and found to be 115·9°C. Other sources report 108°–111°C.,[50] 107·6°C.[143]

The density is given by the equation:

$$d_t = 1{\cdot}6397-2{\cdot}451\times10^{-3}t+1{\cdot}12\times10^{-6}t^2 \qquad (t = -40 \text{ to } 60°\text{C.})^{143}$$

a value of $d_4^{25}$ 1·583 has also been recorded.[54] The viscosity is given by:

$$\log\eta = -1{\cdot}27912+\frac{405{\cdot}35}{T}-0{\cdot}0045507T \qquad (-40 \text{ to } +45°\text{C.})^{143}$$

Other physical data include: m.p. −96·5 ± 1°C.,[54] −91·3°C.[143]; molar heat of evaporation 7925 g.-cal.,[54] 9125 g.-cal.[143]; Trouton constant 20·4,[54] 23·7–24·6.[143]

Qualitatively the anhydrous acid is similar to perchloric and fluorosulphonic acids.[4]

The infra-red spectra in the region 4000–400 cm.$^{-1}$ of liquid and of associated and monomeric gaseous difluorophosphoric acid have been reported and assigned. The free O–H stretching frequencies are at 3662/3679/3694 cm.$^{-1}$.[144]

In common with the other fluorophosphoric acids nuclear magnetic resonance spectra have been examined.[16–8, 98–9] Details are given in Table V.

*Table V.—Nuclear Magnetic Resonance Data for Difluorophosphoric Acid*

| Resonance | Line structure | Applied field (gauss) | Splitting (gauss) | Chemical shift* |
|---|---|---|---|---|
| Fluorine | (1–1) | 6365<br>4180 | 0·244<br>0·242 | $0{\cdot}90\times10^{-5}$ |
| Phosphorus | (1–2–1) | 6365 | 0·570 | $2{\cdot}1\times10^{-5}$<br>$(2{\cdot}01\times10^{-5})$ |

* Referred to trifluoracetic acid and phosphoric acid respectively.

The (1–2–1) structure suggests two fluorine atoms covalently bonded to one phosphorus atom. There seems to be no evidence of any interaction between the two fluorine atoms themselves, although at lower field strengths certain changes in the fluorine doublet take place.[17] At about 500 gauss the doublet is still present but in the vicinity of 237 gauss the two lines coalesce to a single broad line ($\Delta H$ approx. 0·250). However, when the applied field is reduced to as little as 37 gauss,[99] normal splitting is observed, i.e. 0·245 (±0·003). This anomaly at 237 gauss is not understood.

The difluorophosphate anion has $C_{2v}$ symmetry with P–O = 1·470, P–F = 1·575 Å., <F–P–F = 97·1°, <O–P–O = 122·4°, suggesting about 83% double bond character for the P–O bond.[145]

## Chemical Properties

An aqueous solution of difluorophosphoric acid hydrolyzes but when freshly made it behaves as a strong monobasic acid. When titrated with alkali the neutral point occurs at pH 7·3, but the salt produced in solution rapidly hydrolyzes to monofluorophosphate and fluoride.[15]

The nitron salt is precipitated by the acid from cold aqueous solutions of nitron acetate, a property which is useful analytically.[55]

As expected from the equilibria already discussed the mono- or hexa-fluorophosphoric acid can be obtained by the addition of water or hydrofluoric acid respectively. In general mixtures are obtained.[4]

The anhydrous acid attacks most common metals except aluminium, silver and platinum. However if the acid is diluted, aluminium soon dissolves. The corrosion of steel by aqueous solutions of the acid can be inhibited, even at 300°F., by various organic compounds.[106] In the absence of moisture borosilicate glass is resistant provided that the temperature does not exceed 50°C. Normal polymeric hydrocarbons and fluorocarbons, butyl rubber and wax are inert to the acid at ordinary temperatures.[15]

With alcohols the acid yields a *mono*fluorophosphate ester.[15]

Organic applications include the use of the acid as a catalyst for the polymerization of olefines,[21] in the non-oxidizing refinement of oils[12] and, in a boron trifluoride complex, $HPO_2F_2,0{\cdot}5BF_3$, as an alkylation catalyst.[94] Its use as an improver for asphaltic bitumens is claimed.[100] With other fluorophosphoric acids, difluorophosphoric acid has been used to remove the residual sand from metals cast in sand moulds,[23] and to improve the permeability of certain geological formations.[24,103] Several patents[101-2,104-5] have described its role in 'acidizing' oil wells.

## DIFLUOROPHOSPHATES

A difluorophosphate was first obtained in admixture with the monofluorophosphate as a result of fusing phosphorus pentoxide and ammonium fluoride. This is discussed under monofluorophosphates. More generally difluorophosphates may be prepared by neutralizing the acid,[11] provided that adequate precautions are taken to prevent hydrolysis. However they are best prepared by a double decomposition technique. Many organic bases give insoluble crystalline difluorophosphates when their acetates are mixed with dilute solutions of the ammonium salt.[5] Thus tetramethylammonium, strychnine, brucine, morphine, cocaine and nitron salts have been characterized:

$$\underset{\text{nitron acetate}}{C_{20}H_{16}N_4.OOC.CH_3} + NH_4PO_2F_2 \rightarrow$$
$$C_{20}H_{16}N_4.PO_2F_2\downarrow + NH_4OOC.CH_3$$

These salts are easily recrystallized from water, and are convenient starting points for the preparation of alkali metal difluorophosphates which are very soluble. Boiling solutions of nitron difluorophosphate are added to solutions containing the calculated quantities of the metallic nitrates. The resultant mixtures are cooled and kept at 0°C.; insoluble nitron nitrate is filtered off, the filtrate being evaporated to dryness under vacuum. Potassium and cæsium salts have been made in this way. Alkali metal difluorophosphates have also been made by reaction of metal chlorides with difluorophosphoric acid.[145]

A method, which has much in common with that of Hill and Audrieth for monofluorophosphates, has been devised.[56] Hexafluorophosphates are allowed to react with various oxides or metaphosphates at high temperatures in silver or platinum vessels:

$$NaPF_6 + 2NaPO_3 \rightarrow 3NaPO_2F_2$$
$$3KPF_6 + 2B_2O_3 \rightarrow 3KPO_2F_2 + 4BF_3$$

Almost quantitative yields are claimed.[146]

### Physical Properties

From the scanty information available, difluorophosphates have been claimed to resemble both perchlorates and fluorosulphonates in their solubility. Thus a particular metal having a perchlorate of limited solubility also has a difluorophosphate of limited solubility, though almost without exception difluorophosphates are much more soluble than the corresponding perchlorates.[4,93]

The resemblance between the two series of salts does not extend to their crystal habits.[5]

Potassium difluorophosphate is the best characterized salt. It is readily soluble in water, and crystallizes from methanol or aqueous *iso*propanol in colourless orthorhombic prisms. An *X*-ray determination showed that the space group was *Pnma* with $a = 8{\cdot}03_9$, $b = 6{\cdot}20_5$, $c = 7{\cdot}63_5$ A., $Z = 4$, the crystal structure resembling that of barium sulphate.[145] The density is 2·442 g./c.c., molar volume 57·4 c.c./mole, m.p. 255°C., and refractive indices $n\gamma = 1{\cdot}435$, $n\alpha = 1{\cdot}387$.[146] The symmetrical and asymmetrical infra-red absorption frequencies of the $PO_2$ group in sodium and potassium difluorophosphate have been reported, and compared with those in compounds of similar structure.[147]

The infra-red spectrum (Table VI) of ammonium difluorophosphate has been determined.[15,44] This salt forms colourless rhombic prisms, which melt without decomposition at 213°C.

*Table VI.—The Infra-red Absorption Spectrum of Ammonium Difluorophosphate*

| Position of absorption (cm.$^{-1}$) | Intensity |
|---|---|
| 2900–2550 | medium weak |
| $\left\{\begin{array}{l}1445\\1414\end{array}\right.$ | weak<br>strong |
| 1262 | strong |
| 1125 | strong |
| 1005 | very weak |
| $\left\{\begin{array}{l}870\\832\end{array}\right.$ | weak<br>strong |

Nitron difluorophosphate melts at 230·5–232·5°C. (uncorr.) and at 18°C. dissolves to the extent of 1 : 300 in water.[4]

### Chemical Properties

In general difluorophosphates are not very stable. They easily hydrolyze in water, particularly above room temperature or in the presence of ions which can precipitate insoluble compounds.[5] Initially the solutions are neutral but soon become acidic even when stored at low temperatures.

A study[118] of the hydrolysis of difluorophosphate in the temperature range 0°–25°C. has shown the reaction to be of second order. The activation energy and entropy of activation are 14·5 kcal. and $-17{\cdot}8$ e.u. respectively. At higher temperatures (110°–140°C.) the route of hydrolysis is more complex and the experimental results have been interpreted on the assumption that atoms of phosphorus and fluorine are simultaneously attacked by different molecules of water.[119]

Difluorophosphates are readily converted to the corresponding monofluorophosphates, this being a preparative technique for the latter.[6]

It has been claimed that the zinc, cobalt, lead, iron and cadmium salts function as catalysts in the preparation of $\beta$-lactones.[57]

## HEXAFLUOROPHOSPHORIC ACID

Hexafluorophosphoric acid occurs to the extent of about 0·4% in the products of the reaction between phosphorus pentoxide and 40% aqueous hydrofluoric acid, whence it was first isolated as its nitron salt.[58] It is also formed in small quantities by the action of hydrogen fluoride on phosphoryl trifluoride and phosphorus pentafluoride. The presence of some moisture seems to be necessary to promote the reaction with phosphorus pentafluoride[4]:

$$HF + PF_5 \rightarrow HPF_6$$

Products containing as much as 98% of hexafluorophosphoric acid can be prepared by carrying out the above reaction in liquid sulphur dioxide at temperatures in the range $-15°$ to $-30°$C.[63] This reaction can be extended to include other phosphorus halides which may be fluorinated *in situ*, in a diethyl ether medium, by adding excess of hydrofluoric acid. A suspension of red phosphorus has been fluorinated with chlorine trifluoride[120] to give hexafluorophosphoric acid. A liquid product, $HPF_6,2Et_2O$ results, which boils at 114°C. and melts at −35°C.[107]

The acid is more usually prepared[15] by causing anhydrous hydrofluoric acid to react with phosphorus pentoxide in silver or aluminium equipment:

$$P_2O_5 + 12HF \rightarrow 2HPF_6 + 5H_2O$$

operating in a closed system with cooling to prevent loss of volatile material.

By choosing suitable conditions based on the sequence of equilibria already discussed (p. 843) good yields are obtainable:

| Reactants | Mole ratio | Equilibrium concentration of $HPF_6$ |
|---|---|---|
| HF, $H_3PO_4$ | 6:1 | 52·6% |
| HF, $HPO_2F_2$ | 4:1 | 75·0% |

Provided that a fairly concentrated solution of the acid is available, it is possible to deposit hygroscopic crystals of hexafluorophosphoric acid hexahydrate by adjusting the water content of the system to the proper value and cooling the solution rapidly.[4]

As soon as the crystals melt the equilibria are re-established and other fluorophosphoric acids appear as impurities. A typical analysis of commercially available acid is shown in Table VII.

*Table VII.—Typical Composition of Hexafluorophosphoric Acid*[15]

| Component | Percentage |
|---|---|
| $HPF_6$ | 65 |
| HF | 6 |
| $HPO_2F_2$<br>$H_2PO_3F$<br>$H_3PO_4$ | 8 |
| $H_2O$ | 21 |

Hexafluorophosphoric acid has also been prepared by the action of hydrogen fluoride on uranyl phosphates[148] or diphenyl phosphoramidate[149]:

$$(PhO)_2PONH_2 + 7HF \rightarrow 2PhOH + H_2O + NH_4F + HPF_6$$

Aqueous solutions of the acid[121] may be prepared by passing solutions of the sodium salt over a cation exchange resin.

## Physical Properties

Typical samples of hexafluorophosphoric acid are colourless clear liquids which fume considerably. The fuming of a 65% $HPF_6$ solution is comparable with that of 50% HF solution. The hexahydrate melts at 31·5°C. and an octahydrate has been detected.[15]

Nuclear magnetic resonance spectra[16−8,98] suggest that the hexafluorophosphate ion contains six fluorine atoms covalently bonded to a single phosphorus atom. The multiplets, splittings and chemical shifts are listed in Table VIII.

*Table VIII.—Nuclear Magnetic Resonance Data for Hexafluorophosphoric Acid*

| Resonance | Line structure | Applied field (gauss) | Splitting (gauss) | Chemical shift* ($\times 10^{-5}$) |
|---|---|---|---|---|
| Fluorine | (1–1) | 6365 | 0·178 | −0·55 |
| | | 4180 | 0·179 | |
| | | 175 | 0·177<br>(±0·001) | |
| Phosphorus | (1–6–15–20–15–6–1) | 6365 | 0·41 | +14·8<br>(+11·8) |
| | | 275 | 0·406<br>(±0·010) | |

*Referred to trifluoroacetic and orthophosphoric acids respectively.

The nuclear magnetic resonance spectra in deuterium oxide are very similar (chemical shifts $\delta_{\mathrm{F}}=6{\cdot}9$, $\delta_{\mathrm{P}}=145{\cdot}4$ p.p.m., and fluorine coupling constant $J_{\mathrm{P-F}}=711$ c.p.s.).[149]

As anticipated, little change occurs in the splittings as the applied fields are varied over quite a wide range. However if the applied magnetic field is reduced to a very low value, the $^{19}$F doublet loses its symmetry,[92] owing to polarization and proton resonance effects.

The crystal structure of hexafluorophosphoric acid hexahydrate has been elucidated very fully (Fig. 4).[59] The compound crystallizes in a cage-type lattice which is rather different from the clathrate structures of the gas hydrates. The symmetry is cubic, of space group $O_h^9$ $Im3m$. The parameters are $a$, 7·678 A., $Z=2$. The P–F bond lengths are 1·73 A. (cf. 1·58 A. in $KPF_6$).[60] Each phosphorus atom may be considered as in the centre of an octahedron with fluorine atoms at the apices, the whole being enclosed in a cubo-octahedral cage of water molecules probably linked by hydrogen bonds.[11]

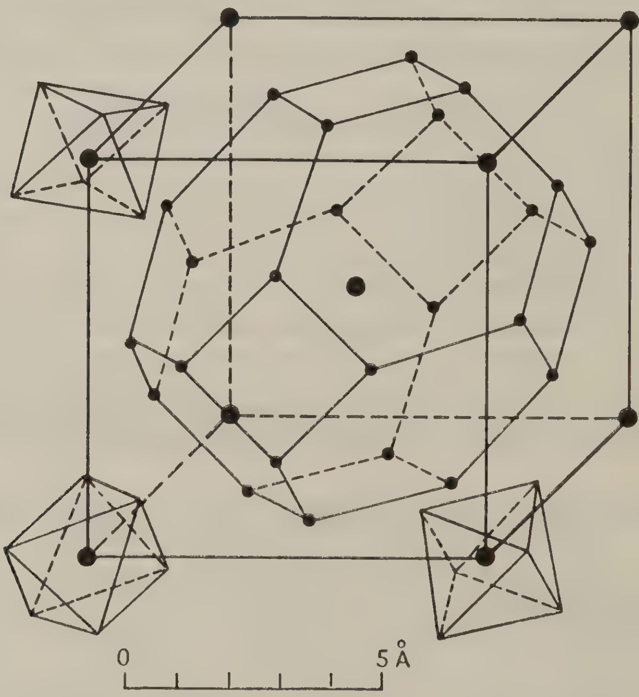


Fig. 4.—Structure of hexafluorophosphoric acid hexahydrate

## Chemical Properties

In the presence of moisture, hexafluorophosphoric acid soon decomposes into a mixture of acids, and the properties of the pure acid cannot therefore be readily investigated. However, it appears to behave as a strong monobasic acid.[15]

The typical mixture attacks nickel, copper and their alloys, lead and stainless steel, if left in contact with these metals. If the mixture is diluted, most metals except aluminium are inert. Silver, platinum, most polyhydrocarbons and polyfluorocarbons, butyl rubbers and wax coatings are not attacked. The anhydrous fluorophosphoric acid does not react with metallic calcium, magnesium, manganese, zinc, chromium or tin[120]; it does however attack silver. Silver fluoride dissolves in the acid to give a colourless solution which deposits silver hexafluorophosphate on evaporation.

Hexafluorophosphoric acid resembles perchloric acid in its behaviour toward sterols.[61] Both acids precipitate colourless crystalline salts from concentrated chloroform solutions of those sterols which contain the 3-$\beta$-hydroxy-$\Delta^5$-ene group.

Many organic bases, such as nitron, also form insoluble salts.[58] Solid adducts are formed between hexafluorophosphoric acid and organic divalent sulphur compounds. The resultant complexes have been applied in the petroleum industry to separate sulphur-bearing materials from hydrocarbons.[108-9]

Salts may be prepared from the acid by straightforward neutralization techniques, although many more efficient methods are available for the preparation of hexafluorophosphates.[15]

The acid can be used in the electrolytic polishing of stainless steels.[62] In common with other fluorophosphoric acids it has found application in the removal of residual sand from metals cast in sand,[23] in the improvement of permeability of certain geological formations,[24] in the 'acidizing' of oil wells,[101-2, 110] and as an improver for asphaltic bitumens.[100]

## HEXAFLUOROPHOSPHATES

Hexafluorophosphates were first obtained by double decomposition reactions in a similar manner to the mono- and di-fluorophosphates.[10, 58] The insoluble nitron hexafluorophosphate is easily precipitated from a solution of the acid and converted into metal hexafluorophosphates, e.g., potassium or barium salts, by treatment with the corresponding nitrates; or into ammonium hexafluorophosphate by the action of ammonia in chloroform. The ammonium salt is a very convenient starting point for many other hexafluorophosphates. Insoluble salts, e.g. those of organic bases, may be precipitated from their acetate solutions. Soluble salts are readily obtained by carefully evaporating to dryness a solution containing ammonium hexafluorophosphate and the appropriate metal hydroxide. Potassium, rubidium, cæsium, sodium and copper hexafluorophosphates have been obtained in this way[10];

$$NH_4PF_6 + NaOH \rightarrow NaPF_6 + H_2O + NH_3$$

If a metal salt is allowed to react with ammonium hexafluorophosphate in the presence of an amine, complex metal ammine hexafluorophosphates are produced, e.g. $Cu(PF_6)_2,5NH_3,H_2O$; $Co(PF_6)_2,6NH_3$; $Ni(PF_6)_2,6NH_3$. The preparation of hexafluorophosphates by this type of reaction is not restricted to the use of the ammonium salt as a starting point, any soluble salt being equally suitable. Thus aryldiazonium hexafluorophosphates have been prepared[15] by precipitation from the appropriate chloride and potassium hexafluorophosphate. Instances of double decomposition reactions in non-aqueous solvents have been recorded, e.g. the reaction of tetramethylammonium hexafluorophosphate with nitrosyl hexachloroantimonate in liquid sulphur dioxide to yield nitrosyl hexafluorophosphate[64]:

$$NOSbCl_6 + (CH_3)_4NPF_6 \rightarrow NOPF_6 + (CH_3)_4NSbCl_6$$

**Refs. p. 868**

On the industrial scale hexafluorophosphates have been prepared by the direct neutralization of the acid with an appropriate base, though the salts prepared in this way, being contaminated by hydrolysis products, must be fractionally crystallized to obtain them in the pure state.[15]

Most other preparative methods described in the literature depend on exhaustive fluorination of suitable phosphorus compounds, usually halides or phosphates. Many fluorinating agents including hydrofluoric acid, metallic fluorides and arsenic and bromine trifluorides, have been investigated. A method that is suitable only for laboratory use consists in heating phosphorus pentachloride with a metallic fluoride at a temperature of 80°–100°C.[65]:

$$PCl_5 + 6MF \rightarrow MPF_6 + 5MCl$$

The reaction product is extracted with water and the nitron salt precipitated. High yields were obtained when potassium fluoride was used. However, with other fluorides yields were lower since the phosphorus pentachloride tended to volatilize before fluorination occurred.

| Fluoride | % Yield |
|---|---|
| Potassium | 80 |
| Ammonium | 67 |
| Sodium | 6 |
| Divalent metals | very low |

It has been suggested that the mechanism of the reaction involves the production of the intermediate pentafluoride, which then combines with the metallic fluoride to give the hexafluorophosphate. Certainly if a metal fluoride is heated in an atmosphere of phosphorus pentafluoride, the following equilibrium is established[4]:

$$KF + PF_5 \rightleftharpoons KPF_6$$

This is also consistent with the recommended modification[66] in which the reaction is carried out in anhydrous hydrofluoric acid. As hydrofluoric acid is such a good fluorinating agent, the metallic chloride may be used and converted to the fluoride *in situ*:

$$MCl + HF \rightarrow MF + HCl$$
$$MF + PCl_5 + 5HF \rightarrow MPF_6 + 5HCl$$

The use of trichloride and liquid chlorine has also been suggested[107] as an alternative to phosphorus pentachloride. Excess hydrofluoric acid is used since this can be driven off subsequently by heating in a current of nitrogen, together with the hydrochloric acid formed as by-product. Substantially theoretical yields of sodium, potassium, ammonium, barium and nitrosyl hexafluorophosphates are claimed, with purities in excess of 95%

Virtually the same reactions occur if bromine trifluoride is substituted for hydrofluoric acid,[67,71] although if phosphorus pentachloride and a metallic chloride are used the hexafluorophosphate is contaminated by the metal bromofluoride. This contamination may be avoided by replacing the pentachloride by the pentabromide.

In non-aqueous solvents phosphorus pentachloride can behave as the salt $(PCl_4)^+(PCl_6)^-$. In these circumstances arsenic trifluoride is able to fluorinate the anion $(PCl_6)^-$.[68] Hence when arsenic trifluoride is added to a solution of phosphorus pentachloride in arsenic trichloride a white hygroscopic salt $(PCl_4)^+(PF_6)^-$ precipitates:

$$2AsF_3 + P_2Cl_{10} \rightarrow 2AsCl_3 + (PCl_4)^+(PF_6)^-$$

In like manner tetrabromophosphonium hexafluorophosphate is precipitated by arsenic trifluoride from a solution of phosphorus pentabromide in carbon disulphide or carbon tetrachloride[69]:

$$2AsF_3 + 2PBr_5 \rightarrow 2AsBr_3 + (PBr_4)^+(PF_6)^-$$

These reactions appear to have a great deal in common with that described above between a metallic fluoride and phosphorus pentachloride, and thus shed a little more light on its possible mechanism. It seems very likely that a similar mechanism also obtains in the reactions of nitrosyl fluoride or dinitrogen tetroxide, with phosphorus pentabromide in bromine trifluoride, which give rise to nitrosyl and nitronium hexafluorophosphates, $NOPF_6$ and $NO_2PF_6$, respectively.[70-1]

Phosphorus (red or white) or phosphorus trichloride reacts with nitrosyl fluoride hydrogen fluoride, $NOF(HF)_3$, to form nitrosyl hexafluorophosphate.[122-4] The same product may be obtained from the reaction of dinitrogen tetroxide, phosphorus pentachloride and hydrogen fluoride. Phosphorus or its pentafluoride reacts with nitryl fluoride to form nitronium hexafluorophosphate[107,125-6]

$$P + 5NO_2F \rightarrow PF_5 + 5NO_2$$
$$PF_5 + NO_2F \rightarrow NO_2PF_6$$

The reaction of chloryl fluoride with phosphorus pentafluoride to give the solid adduct $ClO_2F.PF_5$ (sublimes *in vacuo* at −35°C.) is presumably similar in character.[150] However, the reaction of dioxygen difluoride takes a somewhat different course:

$$O_2F_2 + PF_5 \rightarrow O_2PF_6 + \tfrac{1}{2}F_2$$

Dioxygen hexafluorophosphate, a white solid, is a powerful oxidizing agent. It decomposes rapidly at room temperature, and slowly even at −80°C., giving phosphorus pentafluoride, oxygen and fluorine, according to the equation[151]:

$$O_2PF_6 \rightarrow O_2 + \tfrac{1}{2}F_2 + PF_5$$

Phosphates are readily converted into the hexafluoro-derivatives by the action of bromine trifluoride. The metaphosphates yield reasonably pure metallic hexafluorophosphates, but these are contaminated by bromofluorides if orthophosphates are used.[67,71] The sodium, potassium, silver and barium salts have been prepared in this way. The silver salt has also been prepared from silver powder, phosphoric oxide and boron trifluoride.[152] It reacts with copper powder in boiling toluene, giving silver and a colourless solution of copper(I) hexafluorophosphate which can be kept unchanged, but decomposes on evaporation or treatment with water.[153]

Ammonium hexafluorophosphate has been obtained in a unique reaction between anhydrous hydrofluoric acid and trimeric phosphonitrilic chloride[60]:

$$(PNCl_2)_3 + 18HF \rightarrow 3NH_4PF_6 + 6HCl$$

## Physical Properties

Similarities to perchlorates and halides have been noted. Hexafluorophosphates resemble perchlorates with respect to their solubilities in water and their molecular volumes.[10] In general their solubilities are high except in the case of substituted ammonium salts.[15]

The solubilities of a selection of hexafluorophosphates and perchlorates are given in Table IX.

The ammonium and sodium salts are soluble in organic solvents, e.g., methyl and ethyl alcohol, acetone and methyl acetate.[66] The silver salt also strongly resembles silver perchlorate in being soluble in benzene, toluene, *m*-xylene and mesitylene.[152]

The solubility of potassium hexafluorophosphate in water (see Table X) has been investigated in the range 0–100°C. The equation

$$\log_{10}\frac{1}{N} = -14{\cdot}83906\,\frac{1831{\cdot}26}{T} - 4{\cdot}34237\log_{10}T$$

was found to fit the data very well.[91]

*Table IX.—Solubilities of Hexafluorophosphates and Perchlorates*[4]

| Cation | Hexafluorophosphate (moles/litre of water at room temperature) | Perchlorate |
|---|---|---|
| Potassium | 0·432 | 1·120 |
| Rubidium | 0·076 | 0·071 |
| Cæsium | 0·030 | 0·084 |
| Hexammino-nickel | 0·0018 | 0·0069 |
| Tetramethylammonium | 0·0077 | 0·0652 |
| Benzenediazonium | 0·036 | 0·070 |
| Pyridine | 0·180 | 0·530 |
| Strychnine | 0·0033 | 0·0040 |
| Brucine | 0·0034 | 0·0054 |
| Nitron | 0·0002 | 0·00005 |
| Tetraethylammonium | 0·0294 | 0·1056 |

Freezing-point depressions of hexafluorophosphates and perchlorates[72] indicate further similarities between the two ions.

The refractive indices of both perchlorates and hexafluorophosphates are of the same order. However, there are significant crystallographic differences between the two series of salts. The alkali perchlorates are normally rhombic, whilst the hexafluorophosphates tend to crystallize in the cubic system.[4] Various investigators[73–4] have pointed out the similarity to the alkali halides which also crystallize in a cubic face-centred lattice. Thus crystals of halides and hexafluorophosphates produced by evaporating solutions from freshly cleaved mica surfaces show an oriented growth (epitaxy) which often seems to occur in salts crystallizing with cubic face-centred structures.

*Table X.—Solubility of Potassium Hexafluorophosphate*

| Temperature °C. | % w/w (observed) | % w/w (calculated) |
|---|---|---|
| 0·0 | 3·560 | 3·551 |
| 4·5 | 4·242 | 4·223 |
| 10·5 | 5·270 | 5·255 |
| 16·2 | 6·400 | 6·389 |
| 20·2 | 7·300 | 7·28 |
| 25·0 | 8·35 | 8·45 |
| 30·0 | 9·69 | 9·80 |
| 35·0 | 11·15 | 11·27 |
| 40·0 | 12·85 | 12·87 |
| 45·0 | 14·82 | 14·58 |
| 50·0 | 16·48 | 16·42 |
| 55·0 | 18·22 | 18·35 |
| 60·0 | 20·29 | 20·38 |
| 65·0 | 22·49 | 22·49 |
| 70·0 | 24·61 | 24·69 |
| 75·0 | 27·29 | 26·94 |
| 80·0 | 29·38 | 29·23 |
| 85·0 | 31·96 | 31·57 |
| 90·0 | 34·03 | 33·91 |
| 95·0 | 35·88 | 36·27 |
| 100·0 | 38·30 | 38·62 |

The crystal structures of several hexafluorophosphates have been determined.[60, 75–7] The anhydrous salts of the alkali metals and thallium form primitive cubic unit cells containing four molecules. The metal and phosphorus atoms form a cubic lattice of the sodium chloride type with the fluorine atoms distributed octahedrally around each phosphorus. The unit cell dimensions are tabulated below:

| | A. |
|---|---|
| $NaPF_6$ | 7·61[75] |
| $KPF_6$ | 7·71[60] |
| $NH_4PF_6$ | 7·90[60] |
| $CsPF_6$ | 8·22[60] |
| $TlPF_6$ | 7·49[76] |

At −15·6°C. α-potassium hexafluorophosphate transforms into a rhombohedral β-form of the barium fluorosilicate type having *a* 4·85 A. and α 94°. The energy associated with this phase change is 1·4 g.-cal. per g.,[79] which is consistent with the transition of the $PF_6$ groups from oscillatory motion about the cell diagonal to a stationary state.

The monohydrate of the sodium salt is not cubic but orthorhombic. It crystallizes in colourless prisms of hexagonal habit which show parallel extinction and are optically biaxially negative. Very full structural data have been obtained.[77] There are 4 molecules per unit cell the dimensions of which are *a*, 7962; *b*, 10·594; *c*, 6·116 A. The space group is given as $D_{2h}^{28}$ *Imma* and the positions of the atoms are given in Table XI.

*Table XI.—Atomic Co-ordinates in Sodium Hexafluorophosphate Monohydrate*

| Atom | Number/cell | *x* | *y* | *z* |
|---|---|---|---|---|
| Phosphorus | 4 | 0 | 0 | 0 |
| Sodium | 4 | 0·25 | 0·25 | 0·75 |
| Oxygen | 8 | 0 | 0·25 | 0·52 |
| Hydrogen | 8 | 0 | 0·011 | 0·282 |
| Fluorine (apical) | 8 | 0 | 0·011 | 0·282 |
| Fluorine (planar) | 16 | 0·140 | 1·106 | 0·013 |

The $PF_6^-$ ion in the hydrate is not a regular octahedron as in the anhydrous salts. The P–F distances vary, the four equatorial P–F bond lengths being 1·58 A. while the remaining two at the apices are 1·73 A. It has been calculated[11] that a σ-bond distance corrected for ionic effects would be 1·63 ± 0·02 A., suggesting that the planar bonds have only a small amount of π-character and that the apical bonds are deficient in both σ and π character.

The other interatomic distances are as follow:

| | | | |
|---|---|---|---|
| Na–F (planar) | 2·29 A. | Na–O | 2·44 A. |
| O–F (apical) | 2·90 A. | | |

bond angles are given as:

| | | | |
|---|---|---|---|
| F–HOH–F | 121° | Na–O–Na | 109° |

*X*-Ray powder diagrams have indicated similarities in structure between hexafluorophosphates and hexafluoroarsenates.[68–9] Thus tetrabromophosphonium and tetrachlorophosphonium hexafluorophosphates resemble tetrachloroarsonium hexafluoroarsenate.

The infra-red spectra[78] of several hexafluorophosphates provide evidence of the covalent character of the P–F bonds, which is substantiated by nuclear magnetic resonance data.[11, 16–7]

However, the nuclear magnetic resonance spectra observed[17] for aqueous solutions of potassium hexafluorophosphate were too weak, with an applied field of 6365 gauss, for any conclusions to be drawn about the nature of the fluorine-phosphorus interaction. Nevertheless a fluorine doublet was observable, of splitting 0·176 gauss and chemical shift $-0{\cdot}77 \times 10^{-5}$ p.p.m. measured with respect to trifluoracetic acid.

All the above data are consistent with an octahedral configuration for the hexafluorophosphate ion based upon $sp^3d^2$ hybridization at the phosphorus atom. Analogous alkyl- and aryl-pentafluorophosphates containing ions such as $[CH_3{-}PF_5]^-$ are known,[154] as is the unstable cæsium tetrachlorodifluorophosphate prepared by the reaction[155]:

$$2PCl_2F_3 + 2CsF \rightarrow CsPF_6 + CsPCl_4F_2$$

The densities, viscosities and conductances[127] of aqueous solutions of potassium hexafluorophosphate have been measured at 25° and 40°C. Isopiestic vapour pressure measurements have been made at 25°C. and the osmotic and activity coefficients calculated. The equivalent conductances at infinite dilution are 132·83 and 203·25 cm.$^2$ int. ohm$^{-1}$ equiv.$^{-1}$ at 25° and 50°C., respectively, and the corresponding association constants are 2·42 and 1·43 litres mole$^{-1}$.

The electrical conductivity measurements that have been made[46] at 25°C. show that hexafluorophosphates are strong electrolytes. The equivalent conductance of the potassium salt is $130{\cdot}4 \pm 0{\cdot}5$ ohm$^{-1}$ and the ionic conductance of the $PF_6^-$ anion, 56·9 ohm$^{-1}$. The ionic nature of such compounds as the tetrachloro- and tetrabromo-phosphonium salts is confirmed by conductivity studies in various non-aqueous solvents.[68-9] The values for the equivalent conductances (in nitromethane) of nitrosyl hexafluorophosphate and the corresponding perchlorate lie very close to one another; they are respectively 74·0 and 61·2 ohm$^{-1}$.[64] The heat capacities of ammonium, rubidium and potassium hexafluorophosphate have been measured[128] over the temperature range 20–300°K.

Investigation of the sulphur tetrafluoride–phosphorus pentafluoride system[80] has revealed a certain degree of interaction. It has been suggested that sulphur tetrafluoride tends to form complexes with a higher degree of symmetry than either of the components. Thus a *cis*-cyclic or a *trans*-linear dimer is envisaged, the ligand achieving pseudo-octahedral symmetry by virtue of a lone pair orbital (see Fig. 5). Such a compound would be expected to behave as a salt, $(SF_3)^+(PF_6)^-$.

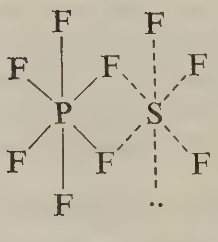


FIG. 5.—Proposed structure of $SF_4$–$PF_5$ complex

### Chemical Properties

Chemically the hexafluorophosphates are relatively inert. This is to a certain extent understandable when the $PF_6^-$ ion is considered in relation to the isoelectronic sulphur hexafluoride molecule which is noted for its inert character. Thus the salts do not decompose spontaneously when dried nor are they sensitive to shock.[10]

The alkali and alkaline earth metal salts dissolve in water to form stable neutral solutions, although if the solution of akaline earth hexafluorophosphate is evaporated, even at very low temperature, it begins to decompose as it approaches saturation.[11] The alkaline hydrolysis of $PF_6^-$[129] takes place at a rate convenient for measurement over the range 160°–190°C. The reaction is of first order with respect to $PF_6^-$ and of zero order with respect to $OH^-$. Its rate is decreased by high concentrations of potassium salts. The hydrolysis takes place by a solvolytic dissociation mechanism, water taking part in the formation of the transition state. The rate of alkaline hydrolysis is increased in the presence of alkali metal ions, their effect increasing in the order $K^+ < Na^+ \ll Li^+$. The temperature dependence of the rate constant is given by the equation:

$$\log 0{\cdot}4343K = 11{\cdot}095 - \frac{6147{\cdot}3}{T}$$

in the range $T = 160°$–191°C. and at an ionic strength of 0·12. The energy and entropy of activation of the process at 175°C. are 28·1 kcal. and −17·0 e.u. respectively. Acid catalysis of the hydrolysis at room temperature is slight. Salts of substituted phosphonium ions are decomposed by water, and must therefore be formed under anhydrous conditions. Tetrabromophosphonium hexafluorophosphate hydrolyzes to yellow-brown solutions with strong oxidizing properties which suggests the formation of bromine together with some lower phosphorus acids.[69] Nitrosyl hexafluorophosphate may be hydrolyzed to the acid and a mixture of nitric oxide and nitrogen dioxide[64]:

$$2NOPF_6 + H_2O \rightarrow 2HPF_6 + NO + NO_2$$

Hexafluorophosphates are easily decomposed by mineral acids, especially when heated,[10] but with alkalis the behaviour varies. In dilute alkaline solutions the salts of the common cations are very stable,[4] although those of somewhat more complex cations are rather less so. Thus the action of alkali on tetrachlorophosphonium hexafluorophosphate decomposes the cation leaving the $PF_6^-$ anion intact:

$$[PCl_4][PF_6] + 7KOH \rightarrow K_2HPO_4 + 5KCl + KPF_6 + 3H_2O \text{ }^{68}$$

However, in the case of tetrabromophosphonium hexafluorophosphate the hydrolysis proceeds further and all the fluorophosphates together with orthophosphate can be detected in the alkaline hydrolysate.[69]

Fusion with caustic alkalis does not normally bring about decomposition of the ion until exceedingly high temperatures are reached.[58]

The action of heat on the hexafluorophosphates usually causes dissociation into phosphorus pentafluoride and a simple fluoride:

$$KPF_6 \rightarrow KF + PF_5 \text{ }^{4}$$

this reaction being the reverse of one of the preparative procedures described above. Dry diazonium hexafluorophosphates decompose harmlessly in a similar manner although the reaction is not reversible[10]:

$$(ArN_2)(PF_6) \rightarrow ArF + PF_5 + N_2$$

As this decomposition takes place at relatively low temperatures, it affords a convenient method for the preparation of phosphorus pentafluoride. Other hexafluorophosphates have been reported to decompose in a somewhat similar manner:

$$\begin{aligned}(PCl_4)(PF_6) &\rightarrow PF_5 + PCl_4F \text{ }^{81}\\ (PBr_4)(PF_6) &\rightarrow PF_5 + PBr_4F \text{ }^{69}\\ NOPF_6 &\rightarrow PF_5 + NOF \text{ }^{64}\end{aligned}$$

The nature of the phosphorus tetrachlorofluoride produced by the thermal decomposition of tetrachlorophosphonium hexafluorophosphate seems to depend on the initial experimental conditions. If the reaction is carried out *in vacuo* the mixed halide is obtained as a homopolar liquid, but in a medium of arsenic trichloride phosphorus tetrachlorofluoride is precipitated as an ionic solid.

Various reactions of a less general nature have been reported. The ammonium salt crystallizes in the presence of ammonium fluoride to yield a double salt, $NH_4PF_6,NH_4F$, which does not melt but sublimes at 140°C.[4] The system, ammonium hexafluorophosphate–ammonia, has been studied tensiometrically in the temperature range $-10°$ to $-70°$C.[20, 111] By varying the composition, pressure and temperature, the following complexes were established:

| *Complex* | *Temperature range* (°C.) |
|---|---|
| $NH_4PF_6,NH_3$ | (−70)–(+28) |
| $NH_4PF_6,2NH_3$ | (−70)–(−15) |
| $NH_4PF_6,4NH_3$ | (−70)–(−33) |

They are stable over the temperature ranges indicated.

Halogen exchange can take place in the cations of the halogen-substituted phosphonium salts:

$$3(PCl_4)(PF_6) + 4AsF_3 \rightarrow 6PF_5 + 4AsCl_3$$ [68]

$$3(PBr_4)(PF_6) + 4AsCl_3 \rightarrow 3(PCl_4)(PF_6) + 4AsBr_3$$ [69]

$$3(PBr_4)(PF_6) + 4PCl_3 \rightarrow 3(PCl_4)(PF_6) + 4PBr_3$$ [69]

In the first case substitution of fluorine for chlorine gives rise to the entity $(PF_4)^+ (PF_6)^-$ which is the ionic form of phosphorus pentafluoride.

The chemistry of nitrosyl hexafluorophosphate has been investigated fairly thoroughly[64, 156] and several reactions have been described:

$$NOPF_6 + C_2H_5OH \rightarrow C_2H_5O.NO + HPF_6$$

$$NOPF_6 + (Me_4N)N_3 \rightarrow N_2O + N_2 + Me_4N.PF_6$$

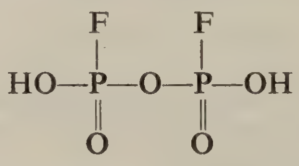
$$NOPF_6 + (Me_4N).SNC \rightarrow NO.SCN + Me_4N.PF_6$$

$$NOPF_6 + BF_3 \rightarrow NOBF_4 + PF_5$$

$$NOPF_6 + ArH + RNH_2 \rightarrow ArR + N_2 + H_2O + HPF_6$$

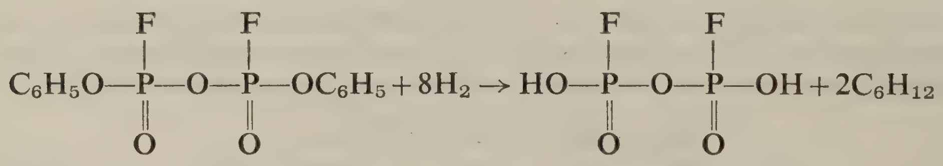
## FLUOROPOLYPHOSPHORIC ACIDS

Although the existence of monofluoropyrophosphoric acid (fluorodiphosphoric acid) has not been established, symmetrical difluorodiphosphoric acid (formulated below) and its salts have been described by several authors.



$$HO-\underset{\underset{O}{\|}}{\overset{\overset{F}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{F}{|}}{P}}-OH$$

The acid is obtained by the hydrogenation of *sym.* difluorodiphenyldiphosphate[157] in ether:

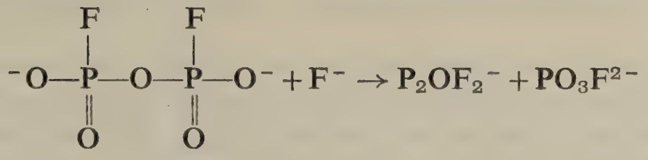


$$C_6H_5O-\underset{\underset{O}{\|}}{\overset{\overset{F}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{F}{|}}{P}}-OC_6H_5 + 8H_2 \rightarrow HO-\underset{\underset{O}{\|}}{\overset{\overset{F}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{F}{|}}{P}}-OH + 2C_6H_{12}$$

It is a viscous, nearly colourless hygroscopic liquid. An attempt[158] to prepare the free acid by the reaction of *sym.* difluorodiphenyldiphosphate with halogen acid was only partially successful, difluorodiphosphoric acid being only one of a number of products.

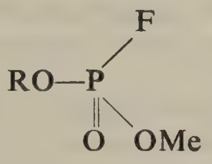
The dilithium salt of the acid has been prepared by reaction of *sym.* difluorodiphenyldiphosphate with lithium chloride in acetone.[158] Alternative methods of preparing the di-alkali metal salts are by the reaction of the metal alkoxide with the acid,[157] the diphenyl ester or the pyridinium salt, $(C_5H_5NH)_2P_2O_5F_2$.[158] The alkali metal salts form colourless crystals.

The ethyl esters of the diphosphoric acids are strong alkylating agents towards alkali and hydrogen halides. The $P_2O_5F_2^{2-}$ ion is comparatively stable in neutral aqueous solution but the P–O–P bridge is split by potassium fluoride[159]:



$$^{-}O-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-O-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-O^{-}+F^{-}\rightarrow P_2OF_2^{-}+PO_3F^{2-}$$

The organic esters are much less stable than the diphosphate ion and react instantaneously with water; they also react with potassium fluoride or silver nitrate to give compounds of the type:



Me = (K or Ag)

The infra-red spectra of disodium and dipotassium difluorodiphosphate have been reported.[147,160] The asymmetrical P–O–P vibrations lie at higher frequencies than in the corresponding pyrophosphates.

Fluoride ions react with trimetaphosphate ions in aqueous solution to yield monofluorotriphosphate:

$$F^{-}+[P_3O_9]^{3-} \rightleftharpoons [P_3O_9F]^{4-}$$

The reaction is reversible, recyclization being more facile in alkaline than in acid solution. At high fluoride concentrations $[P_3O_9F]^{4-}$ is further degraded to $[P_2O_7]^{4-}$ and $[PO_2F_2]^{-}$. Fluorotriphosphoric acid has been isolated in the form of crystalline salts: $(NH_4)_4[P_3O_9F],H_2O$ (plates); $Ag_4[P_3O_9F],H_2O$ (needles); $(Ag, Na)_4[P_3O_9F]$ (Ag/Na = 10·2 : 1 or 8·4 : 1); $(Ag_3K)[P_3O_9F]$ (needles); $Ag_{3\cdot5}(NH_4)_{0\cdot5}[P_3O_9F],H_2O$; $Ba_2[P_3O_9F]$ (long spangles).

Tetrametaphosphate undergoes a similar reaction, especially in concentrated solutions of the ammonium salt:

$$F^{-}+[P_4O_{12}]^{4-} \rightleftharpoons [P_4O_{12}F]^{5-}$$

Like fluorotriphosphate, the fluorotetraphosphate will either recyclize or degrade further to $[P_3O_{10}]^{5-}$ and $[PO_2F_2]^{-}$, according to conditions. Triphosphate also reacts with fluoride ion, but no monofluorodiphosphate has been detected[161]:

$$[HP_3O_{10}]^{4-}+F^{-}\rightarrow [PO_3F]^{2-}+[P_2O_7]^{4-}+H^{+}$$

## ANALYTICAL CHEMISTRY OF THE FLUOROPHOSPHATES

Several physical techniques have been developed for the separation and identification of the fluorophosphates. Paper chromatography has been used[69] with slight modifications[83–4] to the Ebel system normally used to separate condensed phosphates. Electrophoresis using a neutral buffer has also found application.[82] To avoid coincidence of certain spots uranyl and lead salts were added to inhibit the movement of phosphate and monofluorophosphate ions.

It is possible to identify various organic fluorophosphates by microscopical examination,[85] and it is claimed[88] that Raman and infra-red spectroscopy may be used analytically. On the basis of the information[16] obtained from nuclear magnetic resonance spectra, it seems possible that this technique may prove a useful analytical tool in this field. Structural entities in the $HF–P_2O_5–H_2O$ system are recognizable, including a unit hitherto unknown and containing one fluorine atom per phosphorus atom.

**Refs. p. 868**

When mixtures of fluorophosphates are encountered[82] they may be hydrolyzed to orthophosphates and fluorides by digestion with nitric acid. The orthophosphate is separable by ion exchange and the fluoride may be estimated by some standard procedure.

Classical methods for the determination of fluorine such as the precipitation of lead chlorofluoride have been used.[86] Many methods depend on a Willard–Winter distillation followed by a titration or colorimetric finish. Several reagents are bleached by fluoride or fluorosilicate ion, e.g. titanium complexes,[87] or iron salicylate.[89] Free fluoride ion which frequently occurs in samples of fluorophosphates is estimated in this way after removing other salts by precipitation with silver nitrate. A novel method of releasing the fluorine from fluorophosphates, particularly of organic origin, consists of treating the compound with sodium ethoxide at room temperature to liberate sodium fluoride which can be titrated against thorium nitrate using alizarin sulphonate as indicator.[90]

Various gravimetric procedures have been devised[15,86] which rely on the precipitation of very insoluble fluorophosphates themselves. Thus the monofluorophosphate can be precipitated from 80% ethanol solutions by the addition of a suitable silver salt. Nitron acetate precipitates quantitatively both the di-[55] and the hexafluorophosphates. Tetraphenylarsonium chloride has also been used to precipitate the hexafluorophosphate, and to determine it amperometrically.[162]

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### SECTION XXXII

# CHLORINE-SUBSTITUTED OXYACIDS OF PHOSPHORUS

### BY D. A. PALGRAVE

## THE CHLORO-PHOSPHOROUS AND -PHOSPHORIC ACIDS

THE ions corresponding to these acids may be regarded as being derived from phosphite or phosphate by successive replacement of oxygen by chlorine:

| | | | | |
|---|---|---|---|---|
| | $HPO_3^{--}$<br>phosphite | $HPO_2Cl^-$<br>monochlorophosphite | $HPOCl_2$<br>'dichlorophosphine' oxide | |
| $PO_4^{---}$<br>phosphate | $PO_3Cl^{--}$<br>monochloro-phosphate | $PO_2Cl_2^-$<br>dichloro-phosphate | $POCl_3$<br>phosphoryl trichloride | $PCl_6^-$<br>hexachloro-phosphate |

Their existence is not well established, probably because of their relative instability. Dichlorophosphoric acid, as the only member of the series to be isolated, has received the most attention from investigators.

## MONOCHLOROPHOSPHOROUS ACID (Phosphorochloridous Acid)

Investigations[1-2] of the hydrolysis of phosphorus trichloride revealed a previously unknown compound, which was produced in yields up to 75%. Its acidic nature and powerful reducing properties suggested that this entity might be monochlorophosphorous acid, $H_2PO_2Cl$. By carrying out the hydrolysis in ethereal solution, and examining the heat evolved as water was added, the curve shown in Fig. 1 was obtained.[3] The four linear portions on the curves make three intersections which correspond to 1, 2 and 3 moles of water per mole of phosphorus trichloride.

It was claimed on the basis of this work that the hydrolysis of phosphorus trichloride to phosphorous acid involves the production of two intermediates:

$$PCl_3 \xrightarrow{H_2O} P(OH)Cl_2 \xrightarrow{H_2O} P(OH)_2Cl \xrightarrow{H_2O} P(OH)_3$$

Attempts[4] to isolate these bodies by hydrolysis in various solvents at temperatures between $-70°$ and $-20°$C. have so far proved unsuccessful.

## MONOCHLOROPHOSPHORIC ACID (Phosphorochloridic Acid)

Although monochlorophosphoric acid has never been obtained in a pure condition, its existence has been established using nuclear magnetic resonance techniques.[5] By examining the products of the reaction, in a sealed tube at 25°C. and at 100°C., between orthophosphoric acid and phosphoryl trichloride, several species were identified by their chemical shifts measured with respect to 85% orthophosphoric acid in a field of 9395 gauss. The peak at $-18{\cdot}2$ p.p.m. was assigned to monochlorophosphoric acid and that at $-13{\cdot}0$ p.p.m. to a monochlorophosphate end group, $HO(Cl)P(O)O_{1/2}^-$. Monochlorophosphoric acid occurs only when the reagents are present in equimolar proportions. It has been claimed[6] as a hydrolysis product of dichlorophosphoric acid, though no trace of it could be found in the products of hydrolysis of phosphoryl trichloride by varying proportions of sodium hydroxide.[35]

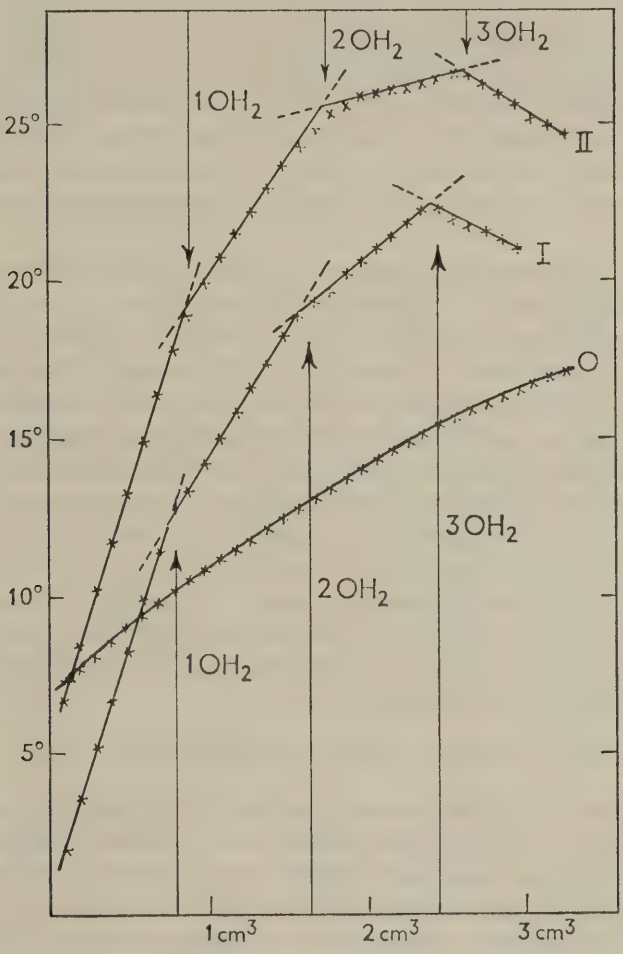
## DICHLOROPHOSPHORIC ACID (Phosphorodichloridic Acid)

### Preparation

Dichlorophosphoric acid was first obtained[7] by hydrolyzing phosphoryl trichloride in an ethereal medium:

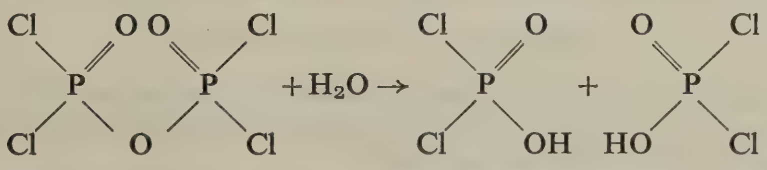
$$POCl_3 + H_2O \rightarrow HPO_2Cl_2 + HCl$$

Later investigators[4] dispensed with the use of ether by working at temperatures between −20° and −10°C. Equimolar quantities of the starting materials resulted in the production of anhydrous dichlorophosphoric acid. If the water content was doubled and the temperature allowed to rise, the monohydrate, $HPO_2Cl_2,H_2O$, was formed. The anhydrous acid has subsequently been prepared[8−10] by the hydrolysis either by water or by alcohols[12−4,24] of pyrophosphoryl chloride at temperatures below −30°C.:



Curves I and II: variations of temperature of ethereal solution of $PCl_3$ as a function of the volume of water added. The arrows indicate the stoicheiometric quantities of water corresponding to the three stages of the hydrolytic reaction.

FIG. 1.—Hydrolysis of phosphorus trichloride



The use of an alcohol yields the corresponding ester as a co-product.

Dichlorophosphoric acid is the main product formed when phosphoryl trichloride is heated with phosphoric acid in a sealed tube between 25° and 110°C., provided that the proportion of the chloride is greater than 50 mole-%.[5] However, free hydrochloric acid and various species including dichlorophosphate end groups, $Cl_2P(O)O_{1/2}^-$, tend to predominate if the concentration of phosphoryl trichloride does not exceed 60 mole-%. At higher temperatures[25] the equilibrium:

$$2POCl_3 + H_3PO_4 \rightleftharpoons 3HPO_2Cl_2$$

is reached quickly, and from stoicheiometric proportions a yield of 93% of the dichlorophosphoric acid is obtained. The reactions:

$$P_4O_{10} + 6H_2O + 8POCl_3 \rightarrow 12HPO_2Cl_2$$

and

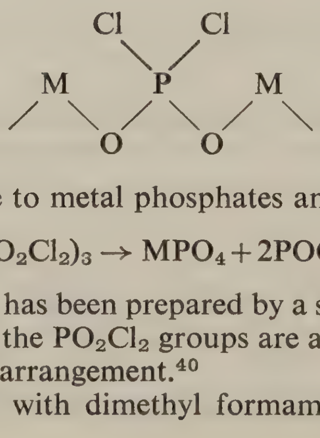
$$P_4O_{10} + 6PCl_5 + 5H_3PO_4 \rightarrow 15HPO_2Cl_2$$

were brought about by heating the reactants at 230°C. in a sealed tube for 72 hr.[5] About 93% of the total phosphorus in the reaction products was present as dichlorophosphoric acid, as estimated by N.M.R. determinations. However, using a different analytical technique,[26] i.e. precipitating the nitron salt of the dichlorophosphoric acid or causing the latter to react with phosphorus pentachloride, it was estimated that not more than 60% of the dichlorophosphoric acid was present in these mixtures.

Salts of common inorganic cations have not been isolated from aqueous solution, although good evidence for the existence of a barium salt in solution[7] was afforded by the data obtained when phosphoryl trichloride or phosphorus pentachloride was titrated with barium hydroxide solution, using thymolphthalein as indicator. When the quantity of base equivalent to barium dichlorophosphate had been added, no precipitation occurred, but at the point corresponding to complete hydrolysis of the starting materials barium phosphate was precipitated. Similarly only mono- and polyphosphates and trimetaphosphates were detected chromatographically among the products of hydrolysis of phosphoryl trichloride by sodium hydroxide solution in molar proportions varying from $POCl_3 : NaOH = 1$ to $100:1$.[36] It should, however, be noted that such condensed phosphates may be artefacts, formed under the conditions of paper chromatography.[37] However in phosphoryl chloride the solvated chlorides $BeCl_2$ and $MCl_3$ ($M = Al, Ga, In, Fe$) react with dichlorine oxide to form the corresponding dichlorophosphates,[39] e.g.,

$$MCl_3 + 3POCl_3 + 3Cl_2O \rightarrow M(PO_2Cl_2)_3 + 6Cl_2$$

These are very hygroscopic compounds, insoluble in non-polar solvents, soluble in dimethyl sulphoxide or dimethyl formamide and violently decomposed by water. All are colourless with the exception of the lemon yellow ferric salt. The dichlorophosphates of gallium, indium and iron are isotypic. The infra-red spectra show that only the beryllium compound is composed of discrete ions, $Be^{2+}$ and $PO_2Cl_2^-$. The trivalent elements, on the other hand, form polymeric structures with oxygen bridges:



When heated they decompose to metal phosphates and phosphoryl chloride:

$$M(PO_2Cl_2)_3 \rightarrow MPO_4 + 2POCl_3$$ [39]

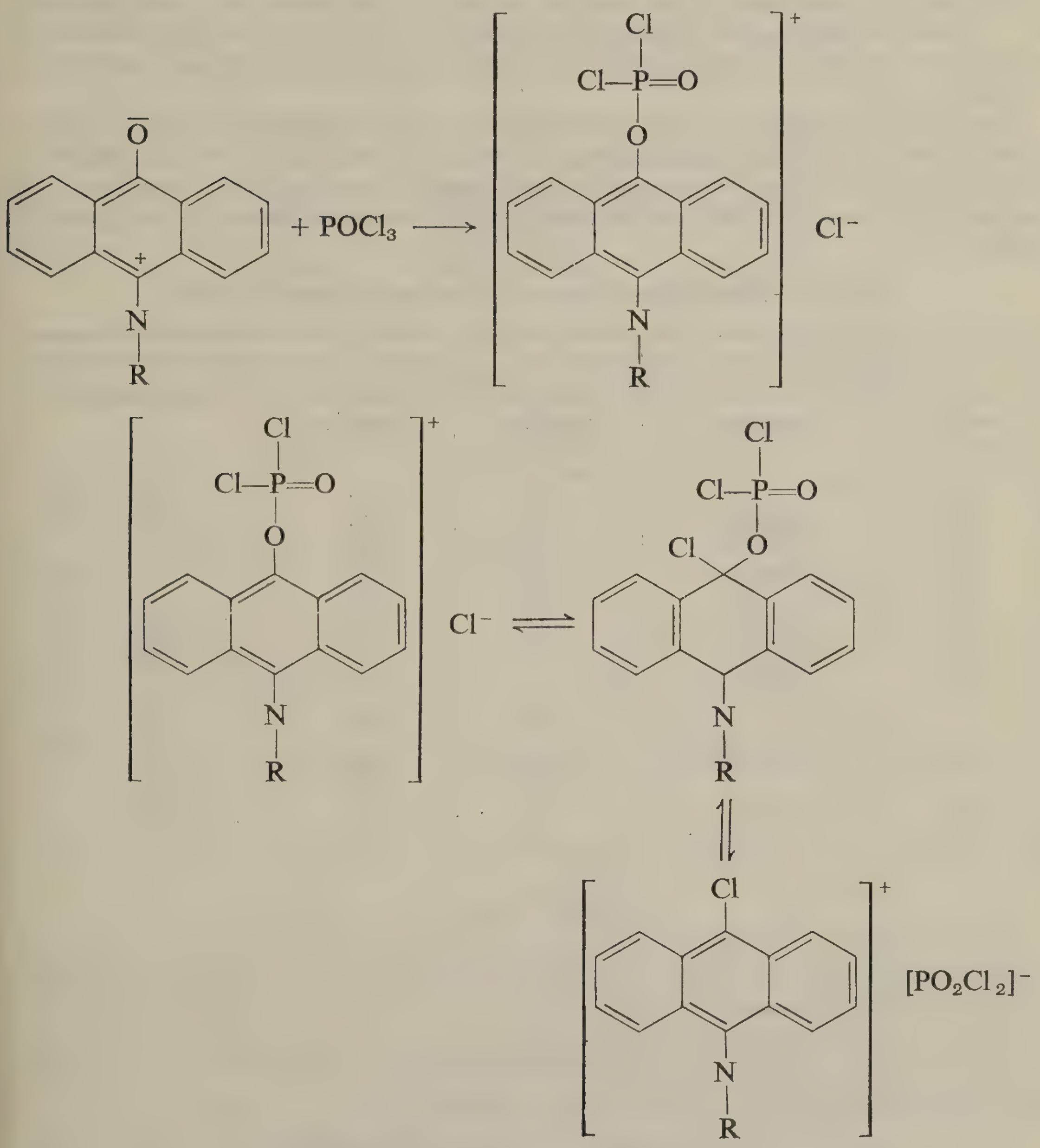
The thallium salt (m.p. 83°) has been prepared by a similar method. This again has a different structure, in which the $PO_2Cl_2$ groups are attached to the central Tl atom in an octahedral chelate-type arrangement.[40]

Phosphoryl chloride reacts with dimethyl formamide in anhydrous acetonitrile giving the crystalline compound $ClCH{=}NMe_2.OPOCl_2$. If treated with sodium perchlorate this yields sodium dichlorophosphate. The tetrachlorostibonium salt, $SbCl_4PO_2Cl_2$ (m.p. 136–8°), can be similarly isolated from the reaction products of $ClCH{=}NMe_2.OPOCl_2$ and antimony(V) chloride in chloroform.[41]

Nitron and brucine salts have been precipitated from solutions of the acid at temperatures in the region of $-15°C$.[4,15] In addition, strychnine and copper ethylenediamine, $[Cu(en)_2]^{++}$, salts have been obtained,[15] although these compounds decomposed on recrystallization.

It has been known for some time[27–8] that certain metal oxides (e.g. those of divalent manganese, zinc, magnesium and calcium) react with phosphoryl trichloride alone, or in solvents such as ethyl acetate, to give complexes containing a metal, phosphorus, oxygen and chlorine. A recent repetition[29] of this work has confirmed the results, the products being crystalline hygroscopic compounds of the formula $MO.P_2O_3Cl_4,(CH_3COOC_2H_5)_2$. *X*-Ray structural determinations on the manganese compound have shown it to be a dichlorophosphate $Mn(PO_2Cl_2)_2,(CH_3COOC_2H_5)$.

An interesting molecular rearrangement results when N-alkylacridones react with phosphoryl trichloride[16]:



The salt-like complexes formed are 9-chloroacridinium dichlorophosphates, and the dichlorophosphate ion is stable enough to survive reaction with other compounds containing active hydrogen atoms to produce well defined 9-substituted acridinium dichlorophosphates,[17] suitable for the characterization of the acridone concerned.

### Physical Properties

Anhydrous dichlorophosphoric acid forms colourless crystalline needles which melt at $-28$°C.[6,8] to a clear mobile liquid having an odour similar to that of phosphoryl trichloride.[5] At 25°C.[5] the density of 93% dichlorophosphoric acid is 1·77 g./c.c., but a more accurate determination using the anhydrous acid yielded the result $d_{25} = 1{\cdot}6878$.[8] The vapour pressure of the 93% material at 25°C. was found to be 17 mm.

Dichlorophosphoric acid is soluble in water and in organic solvents, the solutions in toluene, carbon disulphide, acetone and ligroin being noticeably reddish in colour.[6] It seems probable that reaction occurs on solution in alcohol, with the formation of the dialkyl ester of orthophosphoric acid.[5]

Nuclear magnetic resonance spectra have been examined in a field of 9395 gauss.[5] The position of the chemical shift seems to depend to a certain extent on the ratio of chlorine to phosphorus in the reaction mixture. Thus peaks have been observed at $-9{\cdot}5$ p.p.m. and $-10{\cdot}5$ p.p.m. with respect to 85% orthophosphoric acid. A further peak at $+8{\cdot}3$ p.p.m. has been assigned to the dichlorophosphate end group, $Cl_2P(O)_{1/2}^-$.

The Raman spectra[18] provide evidence of strong hydrogen bonding, with a pronounced effect on the apparent bond orders of the phosphorus–oxygen bonds in the molecule. The effect is weaker if the hydrogen is replaced by deuterium. The spectra of the normal and the deuterated dichlorophosphoric acid are given in Table I.

*Table I.—The Raman Spectra of Dichlorophosphoric Acids*

| $HPO_2Cl_2$ | | $DPO_2Cl_2$ | | Assignment |
|---|---|---|---|---|
| position (cm.$^{-1}$) | intensity | position (cm.$^{-1}$) | intensity | |
| 200 | (8) | 197 | (8) | δ $PCl_2$ ($A_1$) |
| 277 | (4 broad) | 276 | (5) | |
| 342 | (6) | 339 | (6) | |
| 401 | (10 broad) | 392 | (7) | ($A_1$) |
| 501 | (7) | 496 | (8) | |
| 554 | (9) | 547 | (6) | $\nu s$ $PCl_2$ ($A_1$) |
| 595 | (4 broad) | 580 | (3) | $\nu as$ $PCl_2$ |
| 718 | (2) | | | γ OH |
| 986 | (3) | ? | | ν PO |
| | | 1055 | (0) | δ OD |
| 1130 | (2 very broad) | | | δ OH ($A_1$) |
| 1259 | (4 broad) | 1269 | (2) | ν P=O |
| | | 2093 | (0 ?) | ν OD |
| 2819 | (5 broad) | | | ν OH |

### Chemical Properties

Dichlorophosphoric acid is a fairly strong monobasic acid; indeed, it has been claimed that the hydrogen ion is more strongly dissociated than any of the hydrogen ions of orthophosphoric acid.[5] It hydrolyzes in water to give hydrochloric and orthophosphoric acids. The rate of the hydrolysis is similar in acidic and basic solutions, and this, together with the effect of pyridine on the kinetics, suggests that the hydrolysis goes through some such bimolecular mechanism as:

$$HOPOCl_2 \rightleftharpoons H^+ + Cl_2PO_2^- \xrightarrow{H_2O} HCl + HOPClOO^- \quad \text{etc.}^{38}$$

Monochlorophosphoric acid may be formed as an intermediate in the hydrolysis.[6] The acid is quite stable in the absence of air,[8] but decomposes if distilled even *in vacuo*, the main product at 300°C. being pyrophosphoryl chloride with traces of phosphoryl trichloride.[6,9,31] The same result can be achieved by distillation in a stream of hydrogen chloride at 180°C.

Variations in the composition of the products occur if the acid is distilled at ordinary pressures. In general, hydrogen chloride is lost and a condensed phosphoryl chloride produced.[8] The extent of dehydrochlorination depends on the temperature and duration of distillation.[5] At 100°C. a mixture of pyro- and trimeta-phosphoryl chlorides is produced,[6,8] although it has been reported[4] that under these conditions and also at higher temperatures two layers are obtained, the upper consisting of phosphoryl trichloride and the lower of a substance which on further heating yields pyrophosphoryl chloride. In general the residues from these distillations seem to consist of condensed chlorophosphoric acids.

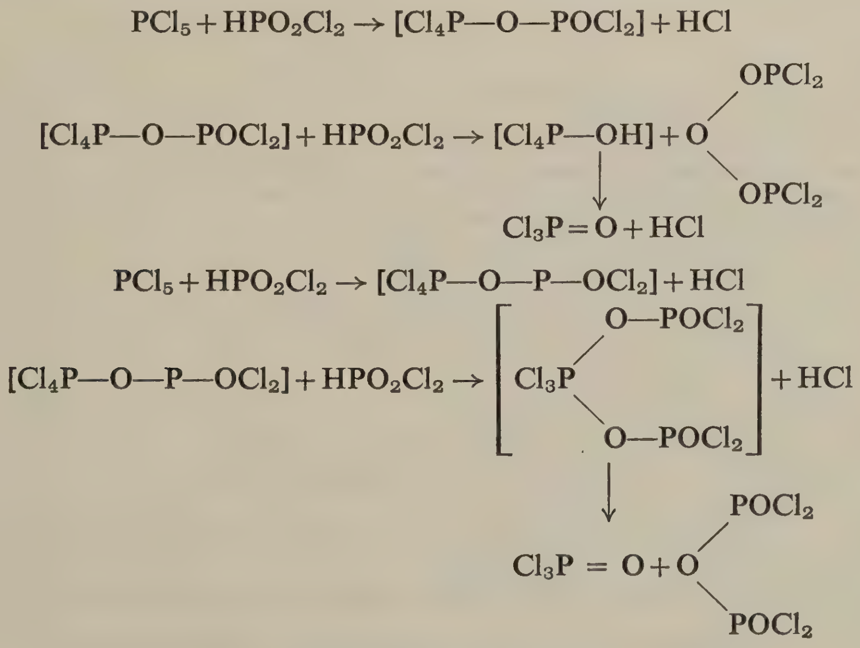
The monohydrate, when kept for about four weeks *in vacuo*, deposits fine crystals of indeterminate composition.[4]

Addition of acid chlorides to dichlorophosphoric acid[25] gives the corresponding anhydrides in the yields listed in Table II.

*Table II.—Reaction of Acid Chlorides with Dichlorophosphoric Acid*

| Acid chloride | Product | Yield % w/w. |
|---|---|---|
| $POCl_3$ | $Cl_2P(O)OP(O)Cl_2$ | 34 |
| $SOCl_2$ | $Cl_2P(O)OSOCl$ | 15 |
| $SO_2Cl_2$ | $Cl_2P(O)OSO_2Cl$ | 19 |
| $Me_3SiCl$ | $Cl_2P(O)OSiMe_3$ | 90 |

Phosphorus pentachloride reacts[30,32] with dichlorophosphoric acid to give pyrophosphoryl chloride possibly by one of the following routes:



$$PCl_5 + HPO_2Cl_2 \rightarrow [Cl_4P\text{—}O\text{—}POCl_2] + HCl$$

$$[Cl_4P\text{—}O\text{—}POCl_2] + HPO_2Cl_2 \rightarrow [Cl_4P\text{—}OH] + O\begin{matrix} \diagup OPCl_2 \\ \diagdown OPCl_2 \end{matrix}$$

$$[Cl_4P\text{—}OH] \downarrow Cl_3P{=}O + HCl$$

or

$$PCl_5 + HPO_2Cl_2 \rightarrow [Cl_4P\text{—}O\text{—}P\text{—}OCl_2] + HCl$$

$$[Cl_4P\text{—}O\text{—}P\text{—}OCl_2] + HPO_2Cl_2 \rightarrow \left[ Cl_3P\begin{matrix} \diagup O\text{—}POCl_2 \\ \diagdown O\text{—}POCl_2 \end{matrix} \right] + HCl$$

$$\downarrow$$

$$Cl_3P = O + O\begin{matrix} \diagup POCl_2 \\ \diagdown POCl_2 \end{matrix}$$

## Dibromophosphoric Acid

Dibromophosphoric acid[33-4] is formed by the controlled hydrolysis of phosphorus oxybromide. The sparingly soluble nitron salt has been prepared by precipitation from a mixture of phosphoryl bromide, acetone and water.

## HEXACHLOROPHOSPHORIC ACID

This acid is known only by virtue of the hexachlorophosphate ion $[PCl_6]^-$. In the phosphorus pentachloride lattice, discrete $[PCl_4]^+$ and $[PCl_6]^-$ ions are postulated (see page 477), and there is abundant evidence of the $[PCl_6]^-$ ion in various non-aqueous solvent systems.[22]

The existence of potassium, cæsium and tetramethylammonium salts with a monovalent cation has been demonstrated by means of conductimetric titrations[19] in iodine monochloride. Similarly, studies of the systems tetramethylammonium chloride–methyl cyanide–phosphorus pentachloride[20] and methyl cyanide–hydrochloric acid–phosphorus pentachloride[21] have established the salts $[Me_4N]^+[PCl_6]^-$ and $[(CH_3CN)_nH]^+[PCl_6]^-$. If phosphorus dichlorotrifluoride is heated for 8 hr. in boiling carbon tetrachloride, a compound is obtained[23] which ionizes in methyl cyanide. Transport measurements indicate an ionic composition of $[PCl_4]^+[PCl_5F]^-$, i.e. tetrachlorophosphonium pentachlorofluorophosphate.

Unstable cæsium tetrachlorodifluorophosphate is formed by the interaction of cæsium fluoride and phosphorus dichloride trifluoride:

$$2PCl_2F_3 + 2CsF \rightarrow Cs^+[PF_6]^- + Cs^+[PCl_4F_2]^-$$

The sparingly soluble cæsium hexafluorophosphate is filtered off, but the filtrate slowly decomposes, yielding more $[PF_6]^-$. Cæsium tetrachlorodifluorophosphate is also very sensitive to moisture.[42]

It seems very likely that the hexachloro- and hexafluoro-phosphate ions are structurally very similar, both being associated with $d^2sp^3$ hybridization at the phosphorus atom. As the sizes of the halide atoms increase, the stability of this type of ion appears to decrease. No hexaiodophosphate is known and the hexabromophosphate ion has only been detected in a solution of phosphorus pentabromide in methyl cyanide[11] (see page 523). The tetrachlorodicyanophosphate ion has been isolated as the tetrapropylammonium and tetrabutylammonium salts (m.p. 157° and 142°C. respectively) from the products of reacting phosphorus pentachloride and potassium cyanide in acetonitrile at 40°–50°C. They are white solids, which slowly evolve hydrogen cyanide when moist.[42]

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## SECTION XXXIII

# THE ORGANIC DERIVATIVES OF PHOSPHORUS

## BY P. A. T. HOYE

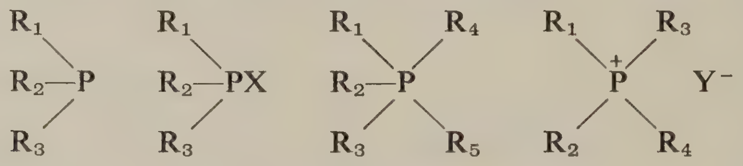
Wöhler in 1828 founded the science of synthetic organic chemistry by his synthesis of urea from ammonium cyanate. Eight years earlier than this Lassaigne[1122] had prepared the first recorded synthetic organophosphorus compounds, crude mixtures of alkyl phosphates, which were made by heating alcohols with syrupy phosphoric acid. Some 20 years later phosphine derivatives were studied by Thénard (cf. ref. 1) and others and since that time the chemistry of organophosphorus compounds has developed at a rapid and accelerating pace.

Although many early workers contributed to the growth of organophosphorus chemistry, it is to the German chemist Michaelis and co-workers that we owe most of the development during the latter half of the nineteenth century. They synthesized vast numbers of organophosphorus compounds, particularly those with carbon–phosphorus bonds, and developed many of the methods of preparation which are in use today. This work was continued and extended by Arbuzov in Russia, particularly in the field of phosphorous acid tri-esters.

During the late 1930's and early 1940's research work in Germany and Great Britain showed that certain organophosphorus compounds are highly toxic and could be used as war gases. This work led, after the 1939–45 war, to the development of a considerable number of compounds of commercial and industrial significance which may be used as insecticides.[1247]

Over the last 10–15 years a number of factors have contributed to the growth of organophosphorus chemistry. Amongst these can be mentioned: (i) the discovery by Wittig that alkylidene phosphoranes react with carbonyl compounds to form olefins, (ii) the realization by physical-organic chemists that organophosphorus chemistry offers a fruitful field for theoretical study and investigation of reaction mechanisms, (iii) the enormous industrial and commercial developments of organophosphorus compounds, (iv) recent advances in physical techniques such as nuclear magnetic resonance, which have provided tools for the investigation of organophosphorus structures,[581] and (v) rapid developments in the biological and biochemical aspects of phosphates in life processes.

Organophosphorus compounds can be represented by the general formulae:



where $R_1$, $R_2$, etc., represent combinations of organic substituents, mercapto, amino, etc., X is O, S, $=NR$, $=CR_2$ and Y an acid radical. The problem of naming the many possible variations is difficult and several nomenclative systems have been used. A system of nomenclature has been agreed between the Chemical Society of Great Britain and the American Chemical Society for compounds which contain one phosphorus atom.[1969] This system is somewhat cumbersome in use and is not entirely free from ambiguities and has been strongly criticized.[2163] Nevertheless it is in general usage in British and American literature and has been adopted in this review. Numerous examples are given in the text.

In view of the long history of organophosphorus compounds it is surprising that many of the standard textbooks of organic chemistry make little or no reference to the subject. The first book entirely devoted to organophosphorus chemistry was published in 1938 by Plets,[2132] and the first such book written in English, *Organophosphorus Compounds*,[1] was published only in 1950. Three further books have been published; these are *Organophosphorus Monomers and Polymers*,[2139] *Methoden der Organischen Chemie*[2] and *Structure and Mechanism in Organo-Phosphorus Chemistry*.[2433] In addition to these a considerable number of book reviews, review articles and essays which are generally devoted to one aspect or class of organophosphorus compounds, have been published. These are referred to in the appropriate sections of the text.

## PHOSPHINES

Phosphines are derivatives of phosphorus hydrides, known and hypothetical, in which one or more of the P–H bonds are replaced by a phosphorus–carbon linkage. Such compounds form an extensive series of highly reactive organophosphorus compounds, which together with their many derivatives embody a considerable proportion of organophosphorus chemistry.

| Known or hypothetical phosphine | Type of known derivatives | | |
|---|---|---|---|
| $PH_5$ | $R_5P$<br>phosphorane | | |
| $PH_3$ | $RPH_2$<br>primary, | $R_2PH$<br>secondary, | $R_3P$<br>tertiary phosphine |
| $P_2H_4$ | $R_2P—PR_2$ | $RHP—PHR$ | |
| $P_nH_{(2n+1)}$ | $P_nR_{(2n+1)}$ | | |
| $(PH)_n$ | $R_4P_4$ | $R_5P_5$ | |

### Phosphoranes

Few compounds having phosphorus bonded to five carbon atoms are reported; all are penta-aryl compounds. Pentaphenylphosphorane was first obtained by Wittig and Rieber[4] by the reaction of tetraphenylphosphonium iodide with phenyl lithium:

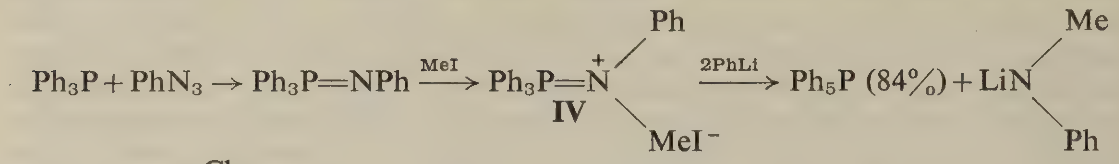
$$Ph_4PI + PhLi \rightarrow Ph_5P + LiI$$

The phosphoranes $(C_6H_5)_4PC(C_6H_5)_3$ and $p$-$CH_3.C_6H_4P(C_6H_5)_4$[6] are prepared similarly.

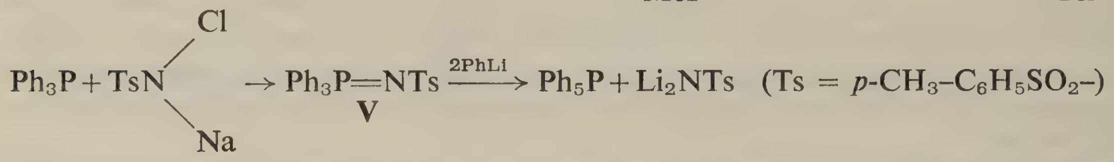
Pentaphenylphosphorane has a measurable dipole moment; *X*-ray analysis shows it to have a trigonal bipyramidal configuration, but the molecule possesses no symmetry owing to asymmetric orientation of the benzene rings[7]; the two P–C axial and three P–C equatorial bond lengths are 1·987 and 1·850 A., respectively.[7]

$Ph_5P$ reacts with hydrogen halides giving tetraphenylphosphonium salts, $Ph_4PX$,[5] and is decomposed thermally giving a mixture of benzene, diphenyl, triphenylphosphine, and a small amount of *P*-phenyl-*o*-diphenylenephosphine (I).[5,8] Initial dissociation to $Ph_4P$– and Ph– radicals has been suggested to account for the variety of products formed when $Ph_5P$ decomposes either by itself or when dissolved in organic solvents such as chloroform, carbon tetrachloride, benzene or pyridine.[8,10] In pyridine, at room temperature, $Ph_5P$ gives a 60% yield of **I** and a trace of 4-phenylpyridine.[8] Equivalence of the five phenyl groups in $C_6D_5(C_6H_5)_4P$ has been demonstrated by reaction with hydrogen bromide.[6,8,9]

Two relatively recent reactions provide a route to a number of novel phenyl *spiro*phosphoranes (II). These are the reactions of an aryl lithium compound with the immonium iodide **IV**, formed by adding methyl iodide to *N*-phenyliminotriphenylphosphorane,[11] or with *N*-(*p*-toluenesulphonyl)iminotriphenylphosphorane **V**[12-3]

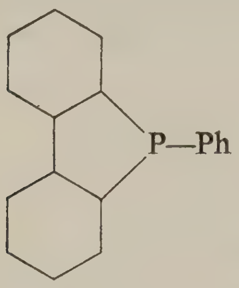


$$Ph_3P + PhN_3 \rightarrow Ph_3P{=}NPh \xrightarrow{MeI} \underset{\mathbf{IV}}{Ph_3P{=}\overset{+}{N}}\begin{smallmatrix}Ph\\ MeI^-\end{smallmatrix} \xrightarrow{2PhLi} Ph_5P\ (84\%) + LiN\begin{smallmatrix}Me\\ Ph\end{smallmatrix}$$

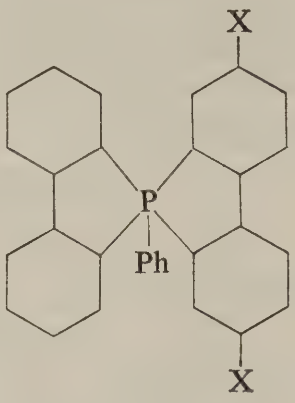


$$Ph_3P + TsN\begin{smallmatrix}Cl\\ Na\end{smallmatrix} \rightarrow \underset{\mathbf{V}}{Ph_3P{=}NTs} \xrightarrow{2PhLi} Ph_5P + Li_2NTs \quad (Ts = p\text{-}CH_3\text{–}C_6H_5SO_2\text{–})$$

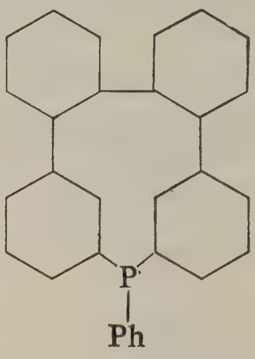
Compounds such as phenyl bis-*o*-phenylenephosphorane, **II**, ($X = H$) are obtained starting from **I** and 2:2′-dilithium diphenyl. At the melting point, compound **II** ($R = H$) decomposes to form phenyl(*o*-tetraphenyl 2′,2′,2′)phosphine, **III**, as the main product.



**I**

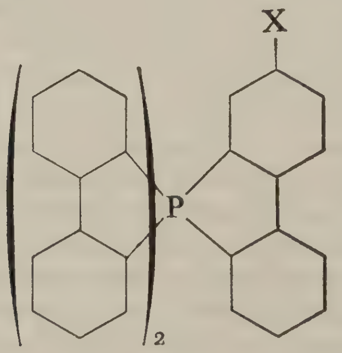


**II** ($X = Me_2N$)



**III**

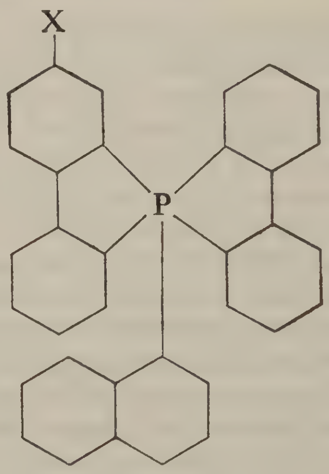
Reaction of phosphorus pentachloride with 2,2′-dilithium diphenyl affords the alkali metal salt of tris(biphenylene)phosphate, **VI** ($X = H$). The octahedral structure of the phosphate anion has been demonstrated by its resolution with brucine methiodide into *d*- and *l*-forms which show extraordinarily high specific rotations. The partially stereospecific acid cleavage of the optically active ate-complexes *d*- and *l*-potassium bis(biphenylene)-4-methylbiphenylene phosphate **VI** ($X = CH_3$) with hydrochloric acid in methanol/acetone led to the first optically active penta-aryl phosphoranes, *d*- and *l*-biphenylene(4-methylbiphenylene)-biphenyl-2-yl phosphorane **VII** ($X = CH_3$). In contrast, acidic cleavage of optically active compound **VI** ($X = H$) affords an optically inactive phosphorane **VII** ($X = H$).[2174-6]
The chemistry of phosphoranes to 1966 is reviewed by Wittig.[2429]



**VI**

$X = H$, $[\alpha]_{578}^{24} = \pm 1930 \pm 30°$

$X = CH_3$, $[\alpha]_{578}^{24} = \pm 1870 \pm 30°$



**VII**

$X = CH_3$, $[\alpha]_{578}^{24} = \pm 94 \pm 1°$

## Derivatives of Phosphine

Simple physical properties of many phosphines are recorded by Kosolapoff[1] and by Houben-Weyl.[2] Vapour pressure data on relatively few phosphines have been determined[39, 210, 242–3, 252] (Table I). Boiling points and heats of evaporation, determined from vapour pressure data, and densities of a large number of phosphines and phosphonous dichlorides are recorded and the boiling points correlated using the quantity $M\rho^2$.[2244]

Electron diffraction study of trimethylphosphine shows the molecule to be pyramidal with a C–P–C bond angle of $100 \pm 4°$ and a P–C bond length of $1{\cdot}87 \pm 0{\cdot}02$ Å.[241, 251]; the molecular weight in the vapour phase indicates a monomeric structure. The heat of formation and the mean dissociation energy of the P–C bonds derived from heat of combustion data are $-30{\cdot}1$ kcal.mole$^{-1}$ and 65·3 kcal. respectively.[253] The crystal structure of triphenylphosphine similarly shows a pyramidal configuration about phosphorus, but owing to unequal rotation of the benzene rings about the P–C bonds the molecule has no symmetry; the P–C bond length is 1·828 Å.[254] The heat of formation, phenyl–phosphorus bond energy, and heat of sublimation of $Ph_3P$ are given as $(Ph_3P, g) = 72{\cdot}4 \pm 2{\cdot}3$ kcal.mole$^{-1}$, $D(P\text{–}Ph) = 70{\cdot}6 \pm 4$ kcal. and $\Delta H_{sub.} = 18{\cdot}1$ kcal.mole$^{-1}$ respectively.[1855]

Many optically active tertiary phosphines have been obtained by Horner and co-workers[33, 41–6] by cathodic reduction of optically active quaternary phosphonium salts at a mercury cathode. Such compounds are optically stable at room temperature and can be distilled under vacuum without noticeable racemization,[45] but racemization occurs if they are heated in solvents. In hydrocarbon solvents the racemization of (+) methyl *n*-propylphenylphosphine follows a first order rate law; the activation energy is 29–31 kcal.mole$^{-1}$.[33, 45] The preparation and reactions of optically active phosphines are reviewed by Horner,[33] who has recently reported the determination of the absolute configuration of ethylmethylphenylphosphine by asymmetric synthesis,[2316] and by Kamai and Usacheva.[2422]

Dipole moments of a number of primary, secondary and tertiary phosphines,[256] and dipole moments and spectroscopic data for a number of arylphosphines and their corresponding oxides and sulphides are recorded.[255, 1705]

Phosphines are basic compounds, forming salts with acids which are structurally analogous to ammonium compounds:

$$R_3P + H^+ \rightleftharpoons R_3PH^+$$

Successive replacement of the hydrogen atoms in phosphine with organic substituents results in a stepwise increase in basicity, the degree of which is determined by the nature of the substituent.[251] Until recently the basicity of relatively few phosphines had been measured and few attempts made to correlate basicity values with structure.[246–7] Streuli[244] measured the basicity of a number of phosphines by potentiometric titration in nitromethane solution (see Table II) and with Henderson[245] demonstrated a correlation of the data with the Taft $\sigma$ values of the substituent groups in the form, $pK_a = A + B\Sigma\sigma$. The results show that the basicity is determined largely by the inductive effects of the substituents. Other factors do operate but are of sufficiently minor importance to enable the $pK_a$ of a phosphine to be predicted to within 1 unit provided the $\Sigma\sigma$ values of the substituents are known. The values of $A$ and $B$ for primary, secondary, and tertiary phosphines are: 2·46, $-2{\cdot}64$; 5·13, $-2{\cdot}61$; 7·85, $-2{\cdot}67$ respectively. Refinements to this method are suggested by Kabachnik and Balueva.[257] Base strengths of a number of phosphines, diphosphines, and aminophosphines, determined by potentiometric titration in aqueous ethanolic solution, are given by Issleib and Bruchlos.[290] $K_b$ values for some hydroxymethyl substituted phosphines are given by Grinshtein *et al.*[2318]

Acid dissociation constants of several primary and secondary phosphines,

$$>P\text{–}H \rightleftharpoons\ >P^- + H^+$$

*Table I.—Vapour Pressures of Some Organic Phosphines*

| Compound | Formula | $\log_{10}p=(-A/T)+B$ | | Heat of vaporization kcal. mole$^{-1}$ | Trouton constant | Boiling point °C./760 mm. | Reference |
|---|---|---|---|---|---|---|---|
| | | *A* | *B* | | | | |
| | $MePH_2$ | | | | | −14 | |
| Dimethylphosphine | $Me_2PH$ | 1370 | 7·539 | 6·27 | | 21·1 | 242 |
| Trimethylphosphine | $Me_3P$ | 1518 | 7·7627 | 6·94 | | 37·8 | 243 |
| | | 1512 | 7·7329 | 6·92 | | 38·4 | 252 |
| Dimethylethylphosphine | $C_2H_5P(CH_3)_2$ | 1712 | 7·850 | 7·83 | | 71·2 | 210 |
| Dimethylvinylphosphine | $(CH_3)_2P(CH{=}CH_2)$ | 1693 | 7·846 | 7·75 | | 69·0 | 210 |
| Triethylphosphine | $(CH_3CH_2)_3P$ | 2065 | 8·035 | 9·45 | | 127·5 | 210 |
| Trivinylphosphine | $(CH_2{=}CH)_3P$ | 1944 | 7·868 | 8·90 | | 58·1/100 mm. | 210 |
| Ethylmethylphosphine | MeEtPH | 1571 | 7·6767 | 7·18 | 21·9 | 54·5 | 39 |
| Methyl-*n*-propylphosphine | $MePr^nPH$ | 1838 | 8·1138 | 8·40 | 23·9 | 78·2 | 39 |
| Methyl-*n*-butylphosphine | $MeBu^nPH$ | 1790 | 7·5210 | 8·18 | 21·22 | 112·69 | 39 |
| Phenylphosphine | $PhPH_2$ | | | | | 55–6/10 mm. | 39 |

*Table II.—Base Strengths of Phosphines*[244]

| Formula | p$K_a$ | Formula | p$K_a$ |
|---|---|---|---|
| $PH_3$ | $-14$[248] | | |
| $C_8H_{17}PH_2$ | $-0{\cdot}02$ | $(CH_3)_3P$ | 8·65 |
| *iso*-$C_4H_9PH_2$ | 0·43 | $(C_2H_5)_3P$ | 8·69 |
| | | (*n*-$C_3H_7)_3P$ | 8·64 |
| $(CH_3)_2PH$ | 3·91 | (*n*-$C_4H_9)_3P$ | 8·43 |
| $(C_6H_5)_2PH$ | 0·03 | (*iso*-$C_4H_9)_3P$ | 7·97 |
| (*n*-$C_4H_9)_2PH$ | 4·51 | (*n*-$C_5H_{11})_3P$ | 8·33 |
| (*iso*-$C_4H_9)_2PH$ | 4·11 | | |
| (*n*-$C_8H_{17})PH$ | 4·41 | $(C_6H_5)_3P$ | 2·73 |
| (*cyclo*-$C_6H_{11})_2PH$ | 4·55 | $(CNCH_2CH_2)_3P$ | 1·36 |
| $(CNCH_2CH_2)_2PH$ | 0·41 | | |

have been determined by Issleib and Kummel by metal hydrogen exchange between substituted alkali phosphide and hydrocarbons, alcohols and amines.[258, 81] Their values are given in Table III below.

*Table III.—Acid Dissociation Constants of Phosphines*

| | p$K_a$ | | p$K_a$ |
|---|---|---|---|
| $PH_3$ | 29 | $Et_2PH$ | 33·7 |
| $PhPH_2$ | 24·5 | $Ph_2PH$ | 21·7 |
| $C_6H_{11}PH_2$ | 32·3 | $(C_6H_{11})_2PH$ | 35·7 |
| | | (*tert*-Bu)$_2$PH | 36·3 |

## Preparation of Phosphines

### FROM ELEMENTAL PHOSPHORUS

Although considerable progress has been made in the synthesis of organophosphorus compounds from elemental phosphorus, the yields which can be obtained are generally poor and, except for a few specific compounds which are otherwise difficult to obtain, synthesis by conventional routes is more satisfactory. The subject has been reviewed by Grayson[20] and by Rauhut.[21]

Hofmann in 1861 obtained $Et_3P$ in low yield by alkylation of white phosphorus with ethyl iodide in the presence of zinc.[14] Complex mixtures of organophosphorus compounds are formed by the action of alkyl iodides on a mixture of white phosphorus and sodium hydroxide solution.[15] Mixtures of tertiary phosphines and phosphonium compounds are formed by heating white phosphorus, olefin, alkyl halide, and hydrogen at high temperatures and pressures.[153] In such reactions, low yields are due to alkylation and halogenation of the intermediate phosphines giving quaternary phosphonium salts and trialkyl dihalophosphoranes respectively; indeed, moderately good yields of tertiary phosphine oxides result from the reaction of phosphorus with alkyl halides either alone[22] or in the presence of iodine or the iodide $P_2I_4$[23, 238] followed by hydrolysis:

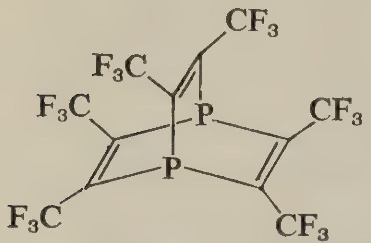
$$RI_{(\text{excess})} + P_2I_4 \rightarrow R_3PI_2 \xrightarrow{H_2O} R_3PO$$

Perfluoroalkyl iodides and white phosphorus form mixtures of the phosphonous di-iodide, phosphinous iodide, and trisperfluoroalkylphosphine, the ratios of which depend on reaction temperatures and time.[154, 240]

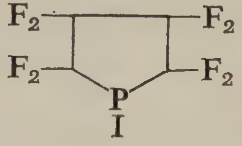
$$CF_3I + P \rightarrow CF_3PI_2 + (CF_3)_2PI + (CF_3)_3P$$

The chemistry of perfluoroalkyl derivatives of phosphorus is reviewed by Banks and Haszeldine.[1313]

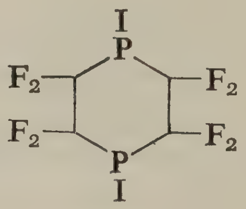
Krespan and co-workers have shown that red phosphorus and bistrifluoromethylacetylene react in the presence of iodine giving the substituted diphosphabi*cyclo*-octatriene, **VIII**,.[152, 264] Tetrafluoroethylene, phosphorus and iodine react to form the cyclic phosphinous iodides **IX** and **X**.[239]



**VIII**



**IX**



**X**

Treatment of white phosphorus with organolithium compounds or Grignard reagents followed by hydrolysis gives small yields of monoalkyl or arylphosphines[18-9]; much of the phosphorus is converted to insoluble substances believed to be organic polyphosphines: phenyl sodium or butyl aluminium gives organopolyphosphines exclusive of monomeric phosphines.[18] Addition of an alkyl bromide to the reaction mixture formed from an aryl lithium or aryl sodium compound and white phosphorus gives isolable products which consist largely of tertiary phosphines, for example:

$$m\text{-}CF_3.C_6H_4Li + P + BuBr \xrightarrow[(2)\,H_2O]{(1)\,Et_2O} m\text{-}CF_3.C_6H_4PBu_2\ (36\%) + (m\text{-}CF_3.C_6H_4)_2PBu\ (37\%)$$

In contrast, the Grignard reagent butyl magnesium bromide, white phosphorus, and butyl bromide react to form tetrabutyl*cyclo*tetraphosphine as the sole major product in up to 42% yield.[18]

Triphenylarsine and phosphorus are reported to undergo exchange at 300° giving $Ph_3P$ and elemental arsenic[16]; tetraphenyl tin reacts with phosphorus at 250° giving a product diphenyltin triphenylphosphine which on oxidation forms diphenyltin oxide and $Ph_3PO$.[17] Small amounts of $PhPH_2$ and $Ph_2PH$ are among the products formed by heating red phosphorus with phenol and water at 250°.[1457]

### FROM METAL PHOSPHIDES

Although the first synthetic phosphines were obtained by passing methyl chloride over heated calcium phosphide,[1] the preparation of phosphines from phosphides has been slow to develop. Inorganic phosphides, such as $Na_3P$ and $Mg_3P_2$, react poorly with alkyl halides owing to their low solubility in organic media. Not until the past few years, with better understanding of the preparation and handling of the alkali metal salts of phosphine and substituted phosphines and their reactions, often in situ in ether solvents, have phosphides emerged as major starting materials for organic phosphines. The preparation, properties and reactions of phosphides and P-substituted phosphides are reviewed by Issleib.[81]

### *Preparation of Phosphides*

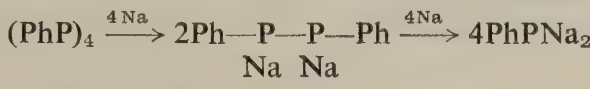
(*a*) Metalation. Alkali metal salts of phosphine are obtained by interaction of phosphine with alkali metals in hydrocarbon solvents,[56] or with sodium emulsion in hydrocarbon–polyglycolether solvent[287] or sodium in liquid ammonia,[52, 64] and by transmetallation with organometallic compounds such as butyl lithium,[57] phenyl lithium[24, 53] or sodium triphenylmethyl.[67] Sodium salts of primary and secondary phosphines are conveniently prepared by using sodium emulsions in hydrocarbon media[51,55] which react with $RPH_2$ at temperatures below 80° and above 95° to give the mono- and the disodium salts respectively,[51] or by using sodamide[56] or sodium in liquid ammonia.[55] Lithium salts are generally obtained by transmetalation reactions with compounds such as phenyl,[24,66,73-4] butyl[62] or methyl lithium[85]:

$$PH_3 \xrightarrow{\text{Na dispersio}} NaPH_2$$

$$RPH_2 \xrightarrow{\text{Na}} RPHNa \xrightarrow{\text{Na}} RPNa_2$$

$$RPH_2 \xrightarrow{\text{2PhLi}} RPLi_2 + 2C_6H_6$$

(*b*) Reduction. Compounds having a P–P or P–Halogen bond are readily cleaved by alkali metals in organic solvents such as dioxan, giving the corresponding phosphides. Examples are the reduction of phosphobenzene, phosphinous halides, and tetra-alkyldiphosphine disulphides:



$$(PhP)_4 \xrightarrow{4\,\text{Na}} 2\,Ph\text{—}\underset{Na}{P}\text{—}\underset{Na}{P}\text{—}Ph \xrightarrow{4\text{Na}} 4PhPNa_2\ ^{38}$$

$$R_2PCl \xrightarrow{2\text{Na}} R_2P\text{—}PR_2 \xrightarrow{2\text{Na}} 2R_2PNa\ ^{25,31,68}$$

$$Et_2PCl \xrightarrow[\text{THF}]{\text{Li}} Et_2PLi\ ^{65}$$

$$R_2PS.PSR_2 \xrightarrow{4\text{Na}} R_2P\text{—}PR_2 + 2Na_2S \xrightarrow{2\text{Na}} 2R_2PNa\ ^{25}$$

(*c*) Cleavage. Tertiary phosphines having at least one aryl substituent are cleaved by metals with loss of the aryl group.[48] Triphenylphosphine can be converted to salts of diphenylphosphine, $Ph_2PM$, by use of lithium in tetrahydrofuran,[26,32,60] sodium or potassium in hot dioxan[70] or by sodium in liquid ammonia[65]:

$$Ph_3P + 2M \rightarrow Ph_2PM + MPh$$

Metal phosphides are readily oxidized by air[55] and react with carbon dioxide[26,77]; they form complexes with dioxan containing 0·2 → 3 moles of dioxan. A number of these complexes, e.g., $(R_2PNa)_2.C_5H_{10}O$, $Ph_2PM.C_5H_{10}O$ ($M = Li$, Na), and $Ph_2PK.(C_5H_{10}O)_2$, have been isolated and characterized by Issleib.[24-5,87] Halogeno–magnesium salts of phosphine and P-substituted phosphines are readily obtained by the action of phosphines on Grignard reagents[54,67,84]:

$$R_nPH_{3-n} + (3\text{–}n)RMgX \rightarrow R_nP(MgX)_{3-n} + (3\text{–}n)RH \qquad (n = 0, 1, 2).$$

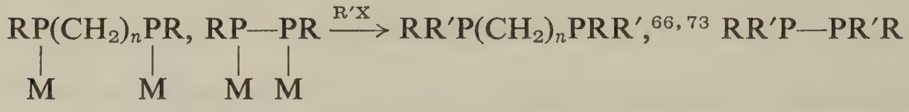
P,P-disubstituted phosphides of magnesium, zinc and a number of heavy metals, $(R_2P)_nM$ ($M = Co$, Ni, Ti(II), V(III), Cr(III)) and mixed metal phosphides $(R_2P)_{n+1}MM'$ ($M = Li$, K; $M' = Mn$, Ni, Cu), have been described.[82,91-3] Their preparation is indicated in the equations below:

$$2R_2PH + MEt_2 \rightarrow (R_2P)_2M + 2C_2H_6 \qquad (M = Mg,^{91}\ Zn^{82})$$
$$nR_2PM + MX_n \rightarrow (R_2P)_nM \qquad (M = Mg, Zn, Co, Ni, V, Cr)$$
$$3LiPR_2 + TiCl_3.3THF \rightarrow Ti(PR_2)_2 + 0{\cdot}5(R_2P)_2\ (R = C_6H_{11})^{92}$$

Phosphides react readily with compounds having a Z-halogen bond (Z = C, Si, Sn, P) with elimination of metal halide and formation of a P–Z bond; they add to carbonyl compounds, olefins, isocyanates, isothiocyanates, and olefin oxides, to form products having a new P–C bond. Solvent and reaction conditions can sometimes markedly affect the nature of the products, e.g., tetraethylethylene-1 : 2-diphosphine is obtained in 94% yield by reaction of $Et_2PLi$ with 1 : 2-dichloroethane in tetrahydrofuran (THF), whereas if the reaction is conducted in ether only ethylene and tetraethyldiphosphine result.[65] The reactions of various phosphides (M = metal) with simple mono- and difunctional alkyl halides (X = halogen) are indicated below. Reactions of monometallic salts of $PH_3$, $RPH_2$, and $R_2PH$, with a number of compounds are indicated in Charts I and II.

$$\mathrm{CaPH} \xrightarrow{R'X} R'_2PH \quad [52]$$

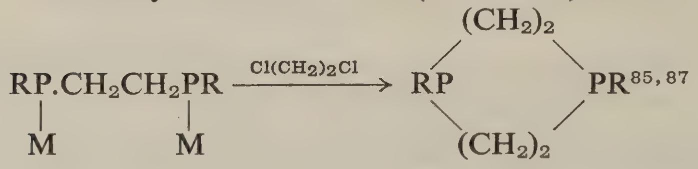
$$PH_2M,\ RPHM,\ RPM_2 \xrightarrow{R'X} R'PH_2,\ [56,67]\ \ RR'PH,\ [51,55-6]\ \ R'_2RP\ [51,55]$$



$$\underset{\substack{| \\ M}}{R}P(CH_2)_n\underset{\substack{| \\ M}}{P}R,\ R\underset{\substack{| \\ M}}{P}—\underset{\substack{| \\ M}}{P}R \xrightarrow{R'X} RR'P(CH_2)_nPRR',\ [66,73]\ \ RR'P—PR'R$$

With polymethylene terminal dihalides, $X(CH_2)_nX$,

| | |
|---|---|
| $PH_2M \rightarrow H_2P(CH_2)_nPH_2$ | $(n = 2, 3, 4, 5)$[64,65] |
| $RPHM \rightarrow RPH(CH_2)_nPHR$ | $(n = 1, 2, 3, 4, 5, 6)$[63-65] |
| | $(n = 3, 4)$[75,76,79] |
| | $(n = 2, R = C_6H_5)$[87] |
| $R_2PM \rightarrow R_2P(CH_2)_nPR_2$ | $(n = 1, 2, 3, 4, 5)$[65] |
| | $(n = 2)$[56] |
| $RPM_2 \rightarrow RP(CH_2)_n$ | $(n = 2, 3, 4, 5, 6, 7)$[64] |
| ↘ | $(n = 4, 5)$[74] |
| Polymers | $(n = 3 \text{ or } 6)$[74] |



FROM ORGANOMETALLIC COMPOUNDS

Tertiary phosphines have been prepared by interaction of phosphorus halides and tertiary phosphites with organometallic compounds of the alkali metals, magnesium, zinc, aluminium, tin and lead.[1,2] By the use of Grignard reagents numerous symmetrical tertiary phosphines, e.g., trialkyl-,[206-7] triaryl-, trisindolyl-,[211] and tris-(trimethylsilyl)methyl-[215] phosphines, have been obtained from phosphorus trichloride; similarly mixed trialkyl, dialkylaryl,[208,216] aryldialkyl, and mixed triarylphosphines may be obtained from phosphonous dihalides or phosphinous halides:

$$PX_3 + 3RMgX \rightarrow R_3P + 3MgX_2$$
$$R'PX_2 + 2RMgX \rightarrow R'R_2P + 2MgX_2$$
$$R'_2PX + RMgX \rightarrow R'_2RP + MgX_2$$

Yields of trialkylphosphines from the Grignard reaction are frequently poor (40–50% for $Bu_3P$) owing to by-product formation of phosphonium salts and amorphous phosphorus. Reactions of the type:[213]

$$Bu_3P + PCl_3 \rightarrow Bu_3PCl_2 + P$$

followed by:

$$Bu_3PCl_2 + RMgX \rightarrow Bu_4PCl + MgCl_2$$

may account for the low yield.

Aliphatic 1,4- and 1,5- diGrignard reagents react with phenylphosphonous

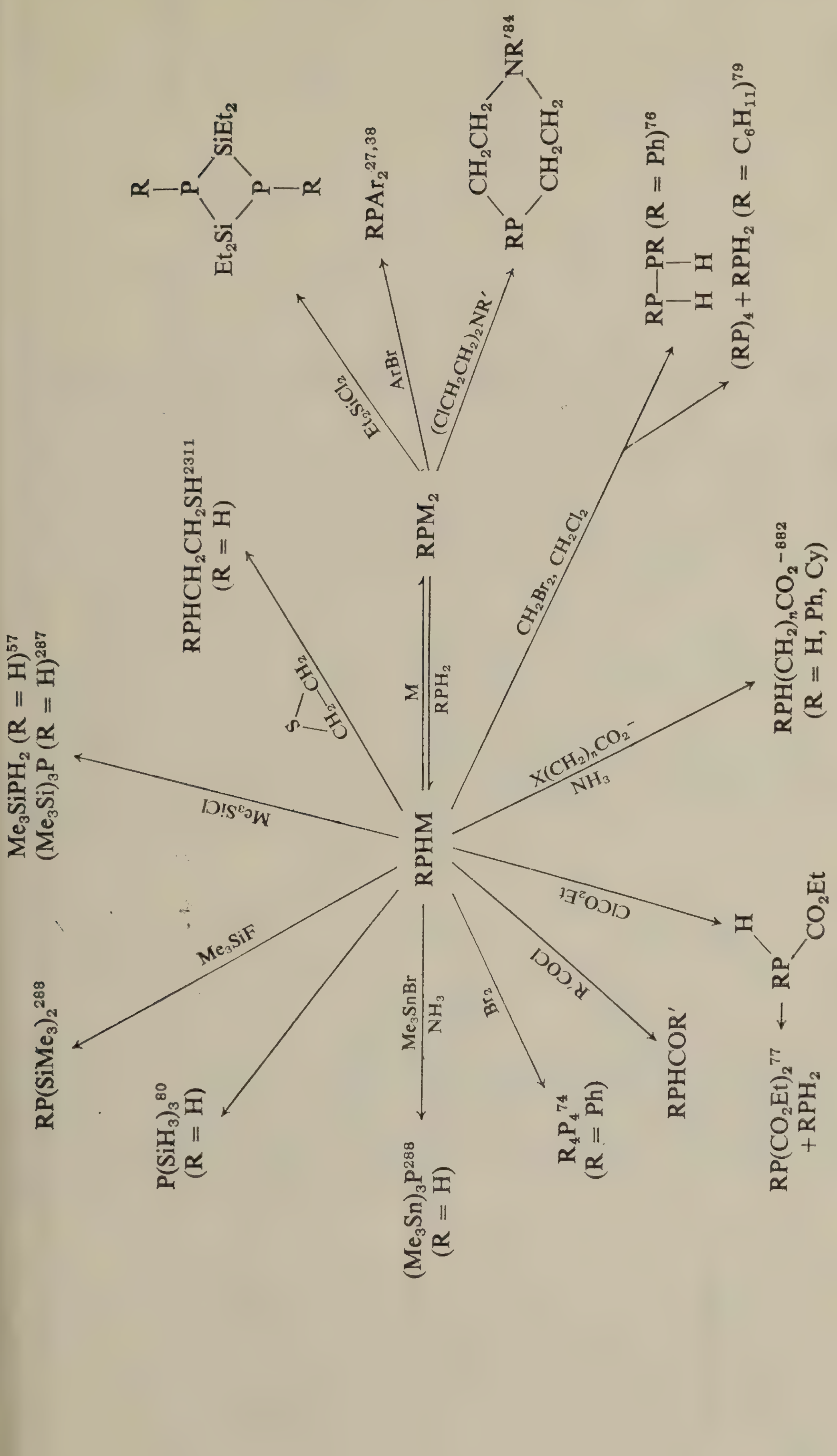


CHART I.—Some reactions of metallic salts of phosphine and monosubstituted phosphines.

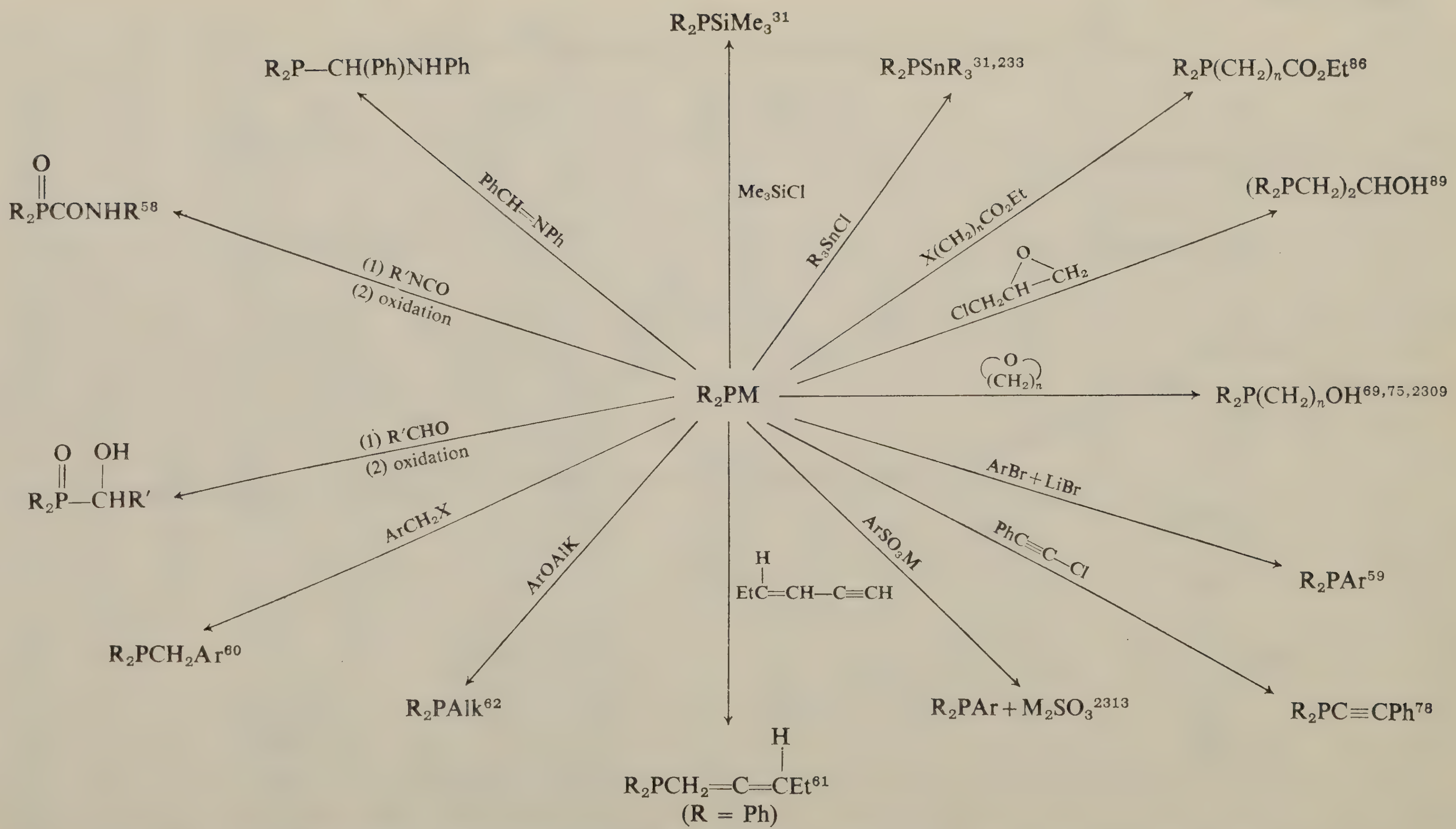
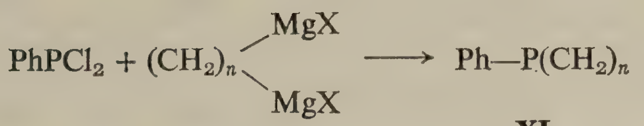
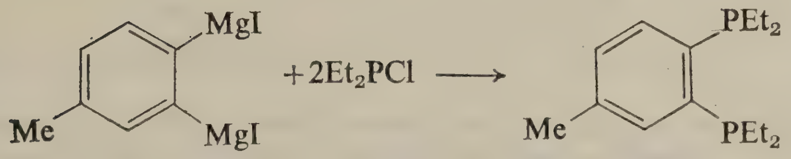


CHART II.—Some reactions of salts of diphenylphosphine (R = monovalent organic group; Ar = aryl group; Alk = alkyl group; M = metal) dichloride to form *P*-phenyl cyclic polymethylenephosphines **XI**.[217] Toluene 3,4-dimagnesium iodide and diethylphosphinous chloride form the diphosphine **XII**.[218]



$$PhPCl_2 + (CH_2)_n\begin{matrix}MgX\\MgX\end{matrix} \longrightarrow Ph—P(CH_2)_n$$

**XI**



**XII**

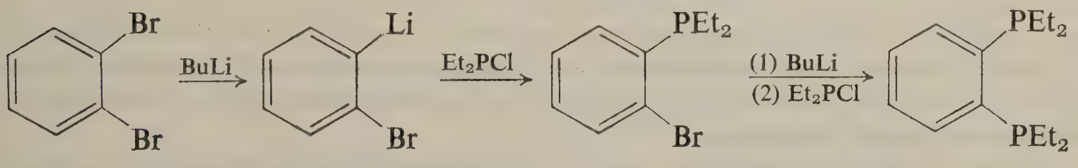
Phosphorus pentachloride and phenylmagnesium bromide form a mixture of diphenyl, triphenylphosphine, triphenyldichlorophosphorane and tetraphenylphosphonium chloride.[231]

Vinyl substituted phosphines, trivinylphosphine,[210,214] vinylalkylphosphines[210] and vinylarylphosphines[98] are obtained using vinylmagnesium chloride. Acetylenic phosphines, $R_2P–C\equiv CPR_2$,[94] $R_nP(C\equiv CR')_{3-n}$ $(n=0, 1, 2)$,[95,6] $R_2P–C\equiv CH$[97] and $Ph_2P(C\equiv C)_nCH_3$ $(n=1, 2, 3)$[2310] are obtained from acetylenic Grignard reagents and the appropriate phosphorus halides. Dialkylethynyl phosphines may be obtained by the reaction of sodium or lithium acetylide with *O*- or *S*-ethyl esters of phosphinous acids in liquid ammonia,[97]

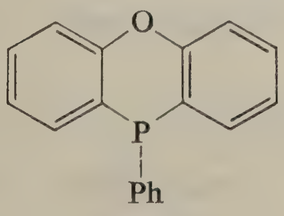
$$EtAPR_2 + R'—C\equiv C^- \rightarrow R'C\equiv CPR_2 + AEt^- \qquad (A=O, S)$$

Mercury phenylacetylide and $PBr_3$ react to form tris(phenylethynyl)phosphine; $PCl_3$ is reported to be unreactive.[95]

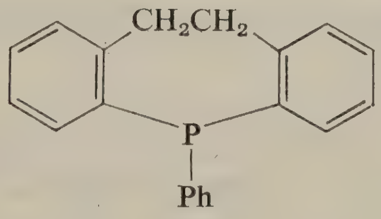
Alkyl[200] or aryl[219-22] lithium compounds react like Grignard reagents with phosphorus halides to replace all the available P–X bonds by P–C bonds. *p*-Dilithiumbenzene and diphenylphosphinous chloride form *p*-bis(diphenylphosphinyl)-benzene.[221] *o*-Phenylenebisdiethylphosphine has been prepared from $Et_2PCl$ and *o*-dibromobenzene[1877]:



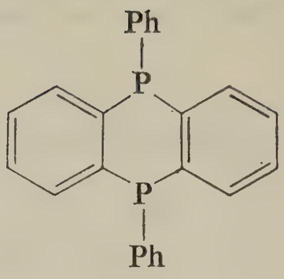
By the use of organolithium compounds a number of novel cyclic phosphines have been obtained; thus phenylphosphonous dichloride reacts with *o,o*-dilithiumdiphenyl ether,[223] *o,o*-dilithium-1,2-diphenylethane,[224] bis(*o*-lithiumphenyl)phenylphosphine,[29] and 1,4-dilithium-1,2,3,4-tetraphenyl butadiene[225-6] giving **XIII, XIV, XV,** and pentaphenyl phosphole **XVI** respectively. The heat of combustion of **XVI** is reported by Bedford and co-workers.[234]



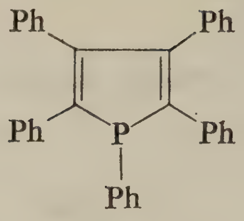
**XIII**



**XIV**

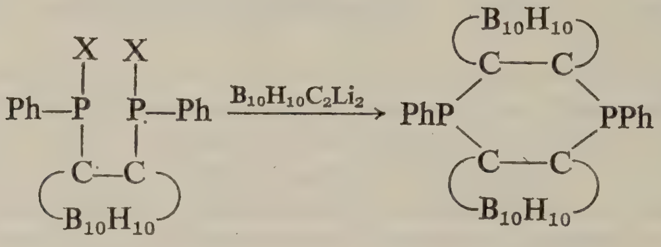


**XV**



**XVI**

Dilithiumcarborane and diphenylphosphinous chloride yield the phosphocarborane (**XVII**, X = Ph), phenylphosphonous dichloride gives the carboranephosphonous chloride (**XV**, X = Cl) which can be converted to the cyclic compound **XVIII**; $PCl_3$ gives a polymeric substance.[227]



**XVII** **XVIII**

One of the earliest methods used to prepare triarylphosphines was the Wurtz reaction[14, 228]:

$$PX_3 + 3ArX + 6Na \rightarrow PAr_3 + 6NaX$$

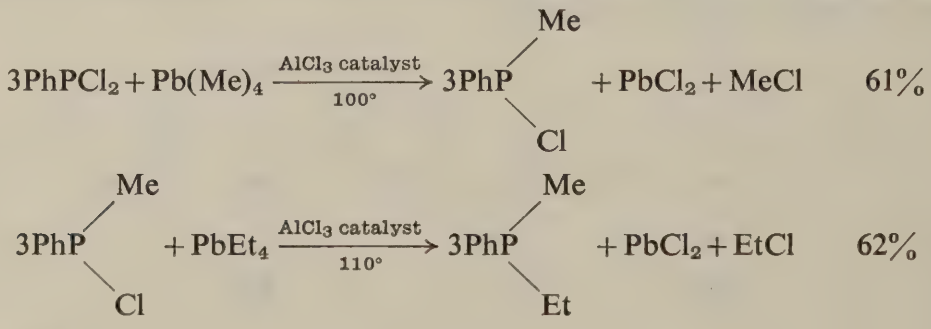
Catalytic amounts of $SbCl_3$ are effective in reactions of halides of low reactivity such as *o*-chlorodiphenyl.[229] Triphenylphosphine is best prepared by the addition of $PCl_3$ to a slight excess of preformed phenyl sodium in a suitable solvent:

$$3PhCl + 6Na \rightarrow 3PhNa + 3NaCl$$
$$3PhNa + PCl_3 \rightarrow PPh_3 + 3NaCl$$

Good yields of trialkylphosphines are reported to result from the reaction of triphenyl phosphite with alkyl halides and sodium in naphtha.[2312] Diphenylphosphinochloridite and sodium or potassium diethyl malonate react to form diphenyl biscarbethoxymethylphosphine.[1565]

Organoaluminium compounds react with phosphorus trichloride giving tertiary phosphines as end products; the yield of $R_3P$ is stated not to exceed about 30% even when an excess of trialkyl aluminium is used.[314]

Organolead compounds react with phosphorous chlorides or bromides to replace one halogen atom by an organic residue. Tertiary phosphines having three different substituents may thus be obtained by successive reactions starting from $PCl_3$[232] or a phosphonous dihalide:

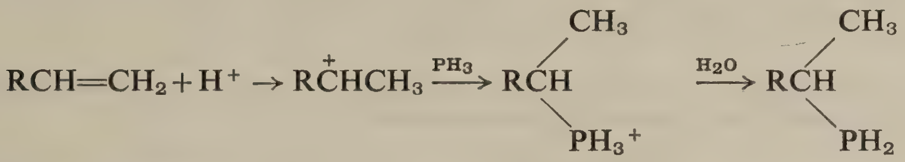


$$3PhPCl_2 + Pb(Me)_4 \xrightarrow[100°]{AlCl_3\ \text{catalyst}} 3PhP\begin{matrix}Me\\Cl\end{matrix} + PbCl_2 + MeCl \quad 61\%$$

$$3PhP\begin{matrix}Me\\Cl\end{matrix} + PbEt_4 \xrightarrow[110°]{AlCl_3\ \text{catalyst}} 3PhP\begin{matrix}Me\\Et\end{matrix} + PbCl_2 + EtCl \quad 62\%$$

### ADDITION REACTIONS

Phosphine adds to olefinic double bonds under a variety of conditions. Olefins, particularly tertiary olefins, react with phosphine under pressure in the presence of nearly stoichiometric amounts of strong non-oxidizing catalysts such as orthophosphoric acid, sulphonic acids or Lewis acids such as $BF_3$-etherate, to form primary phosphine and small amounts of secondary phosphine salts from which the phosphines can be liberated by treatment with water[100-1,145]:



$$RCH{=}CH_2 + H^+ \rightarrow R\overset{+}{C}HCH_3 \xrightarrow{PH_3} R\overset{\displaystyle CH_3}{\underset{\displaystyle PH_3^+}{CH}} \xrightarrow{H_2O} R\overset{\displaystyle CH_3}{\underset{\displaystyle PH_2}{CH}}$$

With free radical catalysts[146-7] or under the influence of ultra-violet light[147-8] the P–H bonds in $PH_3$ react with the double bonds in olefins to give successively the primary, secondary, and tertiary phosphine. By using an excess of either $PH_3$ or olefin the primary or tertiary phosphine can be made to predominate. Radical reactions of organophosphorus compounds are reviewed by Walling and Pearson.[2314]

$$RCH{=}CH_2 + PH_3 \xrightarrow{\text{radical catalyst}} RCH_2CH_2PH_2 \rightarrow (RCH_2CH_2)_2PH \rightarrow (RCH_2CH_2)_3P$$

$$EtCH{=}CH_2 + PH_3 \xrightarrow[\text{16 hours/122C°.}]{\textit{tert}\text{-Butyl peroxide}} Bu_3P$$ [146]

This method, which is probably the most promising general method of combining $PH_3$, $RPH_2$, and $R_2PH$ with olefins has been applied to ethylene, primary, secondary, and tertiary olefins,[147-8,160,164,166,2178] substituted olefins ($CH_2{=}CH{-}CH_2X$, $X = Cl$, OAc, $CO_2R$,[165] OH,[147] $NH_2$[147,165,2308]), fluoro-olefins,[163,167] trimethylallylsilane,[164] vinyltrichlorosilane and methylvinyldichlorosilane.[2306] In the addition of $PH_3$ to fluoro-olefins under the influence of ultra-violet light, addition of the $PH_2$ radical is exclusively to the $CF_2$ group of $CF_2{=}CFCl$ and the $CH_2$ group of $CH_2{=}CF_2$.[163] Tetrafluoroethylene, chlorotrifluoroethylene and 1,1-dichloro-2,2-difluoroethylene react with $PH_3$ to give some 1,2-ethylenediphosphine ($H_2PCX_2CF_2PH_2$, $X = Cl$, F) in addition to the expected products such as $CHF_2CF_2PH_2$ and $(CHF_2CF_2)_2PH$.[163,167] The photochemical reaction of phosphine with trifluoroethylene gives an 85 : 15 mixture of 1,2,2- and 1,1,2-trifluoroethylphosphine.[2307]

The addition of $PH_3$, phenylphosphine, dibutylphosphine, and 2-cyanoethylphosphine, to *cis*-butene-2 is reported to be reversible.[166]

The radical catalyzed addition of phosphines to acetylenic compounds has been briefly examined[160]; bis(2-cyanoethyl)phosphine and octyne-1 give a rather poor yield of bis(2-cyanoethyl)1-octenylphosphine[160]:

$$(CNCH_2CH_2)_2PH + C_6H_{13}C{\equiv}CH \rightarrow (CNCH_2CH_2)_2PCH{=}CHC_6H_{13}$$

Negatively substituted olefins react with phosphine in the presence of strongly basic catalysts giving by successive addition mono-, di-, and tri-$\beta$-substituted phosphines[149,150]:

$$PH_3 + CH_2{=}CHX \rightarrow H_2PCH_2CH_2X \rightarrow HP(CH_2CH_2X)_2 \rightarrow P(CH_2CH_2X)_3 \quad (X = CN,\ NO_2,\ CO_2R,\ CONH_2)$$

Phenylphosphine and diphenylphosphine undergo this reaction at elevated temperatures in the absence of added catalyst[151,161]; phosphine itself and fluoro-olefins react similarly[167]:

$$PhPH_2 + CH_2{=}CHX \xrightarrow{\Delta} PhP(CH_2CH_2X)_2 \qquad (X = CN,\ CO_2Me)$$

Phosphines add to aryl *iso*cyanates in the presence of basic catalysts giving *N*-arylcarbamoylphosphines,[156–7,168,200–1] and benzylideneaniline.[162] Phenyl *iso*thiocyanate is reported to react with primary and secondary phosphines giving *N*-phenylthiocarbamoyl substituted tertiary phosphines, but not with phosphine itself[203]:

$$R_nPH_{(3-n)}+(3\text{–}n)ArNCO \xrightarrow{\text{base}} R_nP(CONHAr)_{(3-n)} \qquad (n = 0, 1, 2)$$

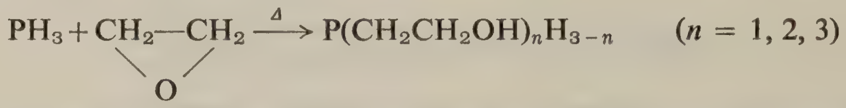
$$R_nPH_{(3-n)}+(3\text{–}n)PhNCS \xrightarrow{\Delta} R_nP(CSNHPh)_{(3-n)} \qquad (n = 1 \text{ or } 2)$$

$$PhPH_2+PhCH\!:\!NPh \rightarrow C_{38}H_{29}N_2P$$

Primary and secondary phosphines, but not phosphine itself, react with cyanic acid, generated *in situ* to form carbamoyl phosphines[2317]:

$$R_nP(CONH_2)_{3-n} \qquad (n = 1, 2)$$

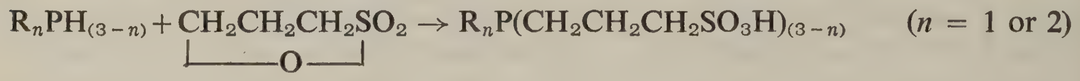
Epoxy-alkanes and phosphine undergo condensation at elevated pressure and temperature without catalyst to form a mixture of mono-, bis- and tris-β-hydroxyethylphosphines,[159] and with catalysts such as $BF_3$-complexes to form tertiary phosphine derivatives of hydroxypolyethers.[158] Dialkylaminoethylphosphines are readily prepared by the Mannich reaction of phosphines with formaldehyde and a secondary amine or with a tetra-alkylmethylenediamine[281,2178]:



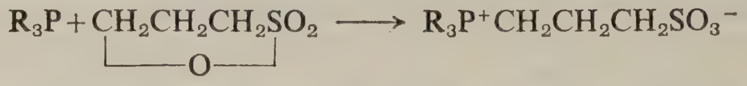
$$PH_3+\underset{\diagdown\;O\;\diagup}{CH_2\text{—}CH_2} \xrightarrow{\Delta} P(CH_2CH_2OH)_nH_{3-n} \qquad (n = 1, 2, 3)$$

$$R_nPH_{(3-n)}+(3\text{–}n)(R_2'NH+CH_2O) \rightarrow R_nP(CH_2NR_2')_{3-n} \qquad \begin{matrix}(R = \text{alkyl, aryl})\\(n = 0, 1, 2)\end{matrix}$$

Sultones react with primary and secondary phosphines giving phosphinosulphonic acids, while tertiary phosphines form quaternary phosphonium betaines[292]:



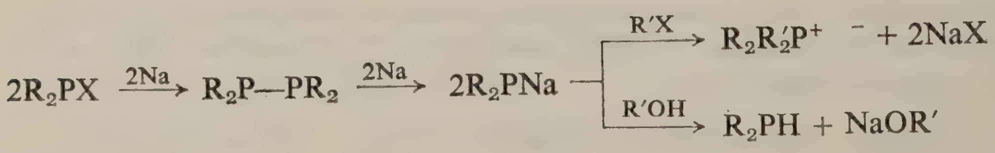
$$R_nPH_{(3-n)}+\underbrace{CH_2CH_2CH_2SO_2}_{O} \rightarrow R_nP(CH_2CH_2CH_2SO_3H)_{(3-n)} \qquad (n = 1 \text{ or } 2)$$



$$R_3P+\underbrace{CH_2CH_2CH_2SO_2}_{O} \longrightarrow R_3P^+CH_2CH_2CH_2SO_3{}^-$$

REDUCTION OF ORGANOPHOSPHORUS COMPOUNDS

The preparation of phosphines by the reduction of compounds having at least one carbon–phosphorus bond has achieved importance only during recent years. The classical methods of reduction used in organic chemistry have proved of little value for reducing pentavalent phosphorus compounds to trivalent ones or for reducing the trivalent ones to phosphines. Reduction of oxides, sulphides, acids, esters, and halides of organophosphorus compounds to phosphine has been accomplished in good yield by use of the more electropositive metals and metal hydrides, particularly lithium aluminium hydride.[28–9,50,71] Metal reductions give the metal salt of the phosphine which may be isolated,[25] reacted *in situ*,[26–7,31,36] or treated with an aqueous reagent to yield the phosphine:



$$2R_2PX \xrightarrow{2Na} R_2P\text{—}PR_2 \xrightarrow{2Na} 2R_2PNa \begin{cases} \xrightarrow{R'X} R_2R_2'P^+ \;\; {}^- + 2NaX \\ \xrightarrow{R'OH} R_2PH + NaOR' \end{cases}$$

Compounds containing oxygen are less readily reduced by metals than the chlorides[36] and have frequently been converted to chlorides or sulphides before reduction:

$$R_3PO \xrightarrow{P_2S_5} R_3PS \xrightarrow{\text{metal}} R_3P$$

$$R_2PO_2H \xrightarrow{PCl_5} R_2PCl_3 \xrightarrow{\text{metal}} R_2PH$$

Optically-active tertiary phosphines are obtained by cathodic reduction of optically-active quaternary phosphonium salts.[41-6]

By reducing phenylphosphonous dichloride with one molar equivalent of $LiBH_4$ the intermediate phenyl chlorophosphine was obtained as an unstable adduct, $PhPHClBH_3$.[72]

Table IV shows the various types of organophosphorus compounds used to prepare primary, secondary and tertiary phosphines, together with the reducing agent employed.

*Table IV.—Preparation of Phosphines by Reduction*

| Product | Source of organophosphorus compound |
|---|---|
| $PH_3$ | $PCl_3$ (Na[36]), $PCl_5$ ($LiBH_4$, $LiAlH_4$[37]) |
| $RPH_2$ | $RPCl_2$ (Li,[27] Na,[36,50] $LiAlH_4$,[28-9,50] $LiBH_4$[72]) |
| | $RPOCl_2$, $RPO(OR')_2$, $RPO_2H_2$ ($LiAlH_4$,[50,2187] LiH,[71] Na,[28] silanes[1610]) |
| | $(PhP)_4$ ($LiAlH_4$,[50] Na[38]) |
| $H_2P(CH_2)_nPH_2$ | $(CH_2)_n[PO(OR)_2]_2$ ($LiAlH_4$[2178]) |
| $R_2PH$ | $R_2PCl_3$, $R_2POCl$, $R_2P(O)OR$, $R_2POH$, $R_2PO_2H$ ($LiAlH_4$[28,90]) |
| | $R_2PCl$ (Na,[36] $LiAlH_4$,[28] Li[65]) |
| | $R_2P(S)P(S)R_2$ (Cu or Raney $Cu/H_2$,[30] Na,[25] $LiAlH_4$[34,39]) |
| | $R_2P{-}PR_2$ (Na[25,31]) |
| | $R_2P(O)OR$, $R_2POCl$ (silanes and $Cl_3SiH$[1610]) |
| | $R_2P{-}Ar$ (Li, Na, K, $Na/NH_3$ removes Ar-group[26,32,60,48]) |
| $R_3P$ | $R_4P^+X^-$ (cathodic reduction at Hg cathode[41-7,117]) |
| | $R_3P^+CH_2PhX^-$ ($LiAlH_4$ removes $PhCH_2$-group selectively[35,2001]) |
| | $R_3PO$ ($CaH_2$,[40] $SiHCl_3$,[1982] polymethyl siloxane,[40] $LiAlH_4$,[28] Na,[28] $Ca(AlH_4)_2$,[49] boranes and trialkylamine boranes) |
| | $R_3PX_2$ ($LiAlH_4$, Na[28]) |
| | $R_3PS$ (Raney Ni, Na, NaH,[28] Fe,[82] $LiAlH_4$, $Ca(AlH_4)_2$[49]) |

### DECOMPOSITION REACTIONS

Quaternary phosphonium halides decompose, usually at temperatures above 200°, giving tertiary phosphines[266-8,271,285]:

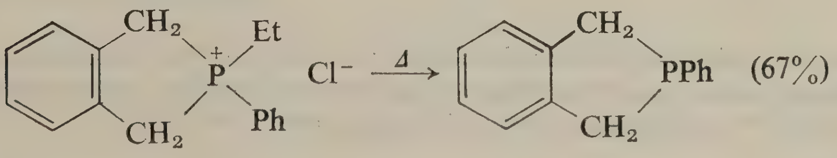
$$R_1R_2R_3R_4P^+X^- \rightarrow R_1R_2R_3P + R_4X$$

The ease of radical cleavage increases in the series:

phenyl < *iso*amyl < propyl < methyl < benzyl < ethyl[267]

However, radical cleavage from an unsymmetrical phosphonium salt is generally insufficiently specific to prevent the formation of a mixture of phosphines, and successful synthetic applications have been made only by eliminations from compounds containing groups such as phenyl and ethyl at the opposite ends of the cleavage order. Examples are the preparation of ethylbenzylphenylphosphine[271] and 2-phenyl*iso*phosphindole[272]:

$$Et_2\overset{+}{P}PhBz\overset{-}{Cl} \xrightarrow{\Delta} EtBzPhP + Et_2PPh$$

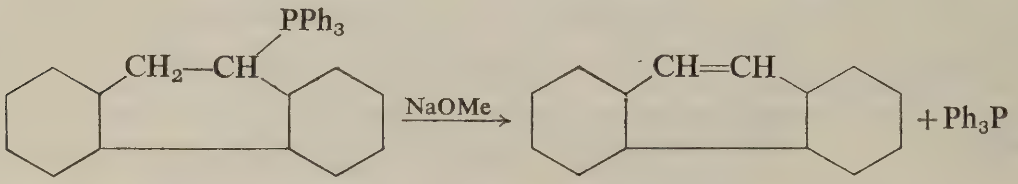


The majority of phosphonium compounds are decomposed by bases to form a tertiary phosphine oxide and a hydrocarbon (paraffinic degradation).[267] A few classes of compounds, notably those containing a 2-cyanoethyl substituent,[270] a hydroxymethylsubstituent,[273, 275–7, 279] a $\beta,\beta$-diphenylethyl substituent,[269] compounds having three or four chloromethyl substituents[274, 276] attached to phosphorus and 9:10-dihydrophenanthrene-10-triphenylphosphonium bromide[278] are readily cleaved by bases to form tertiary phosphine:

$$RP(CH_2CH_2CN)_3X \xrightarrow{NaOMe} RP(CH_2CH_2CN)_2 + MeOCH_2CH_2CN \qquad (R = \text{alkyl or aryl})$$

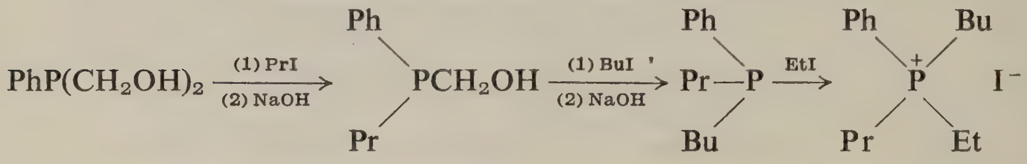
$$RP(CH_2Cl)_3Cl \xrightarrow{NaOH} RP(CH_2Cl)_2 + CH_2O \qquad (R = CH_2Cl, Ph, Et)$$

$$R_nP(CH_2OH)_{4-n}Cl \xrightarrow{base} R_nP(CH_2OH)_{3-n} + CH_2O \qquad (n = 0, 1, 2, 3)$$



Unsymmetrical tertiary phosphines and phosphonium salts have been prepared by successive quaternization and base decomposition of hydroxymethylphosphines[276]:

$$PhPH_2 \xrightarrow[CH_2O]{H^+} PhP(CH_2OH)_3Cl \xrightarrow{NaOH} PhP(CH_2OH)_2$$



$$PhP(CH_2OH)_2 \xrightarrow[(2)\ NaOH]{(1)\ PrI} \overset{Ph}{\underset{Pr}{PCH_2OH}} \xrightarrow[(2)\ NaOH]{(1)\ BuI} Pr{-}\overset{Ph}{\underset{Bu}{P}} \xrightarrow{EtI} \overset{Ph\quad Bu}{\underset{Pr\quad Et}{\overset{+}{P}}} \quad I^-$$

Similar reactions starting from tris(2-cyanoethyl)phosphine afford alkylbis(2-cyanoethyl)phosphine, dialkyl-2-cyanoethylphosphine and tetrakis(2-cyanoethyl)-ethylenediphosphine[270]:

$$2P(CH_2CH_2CN)_3 + XCH_2CH_2X \rightarrow [(CNCH_2CH_2)_3\overset{+}{P}CH_2]_2X^- \xrightarrow{NaOMe} [(CNCH_2CH_2)_2PCH_2]_2$$

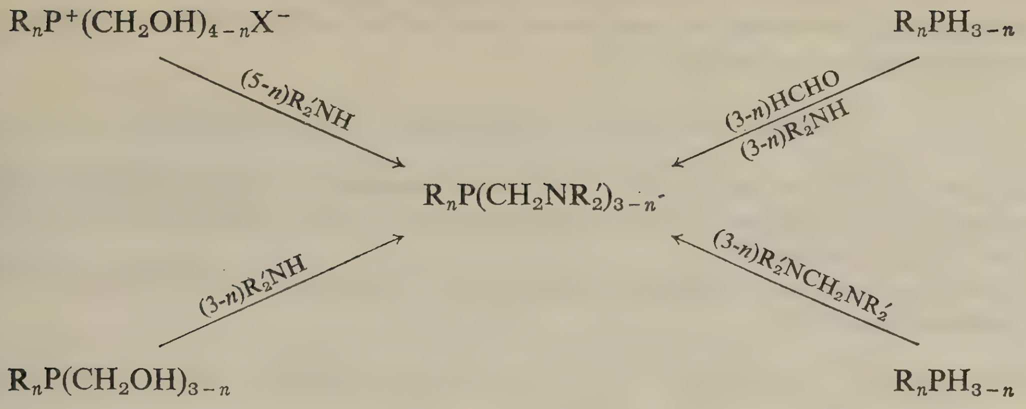
A novel quaternization-decomposition reaction is that of trishydroxymethylphosphine with unsaturated nitriles such as acrylonitrile to form, e.g., tris(2-cyanoethyl)-phosphine[286]:

$$P(CH_2OH)_3 + CH_2{=}CHCN + H_2O \rightarrow (CH_2OH)_3\overset{+}{P}CH_2CH_2CNOH^- \rightarrow (CH_2OH)_2PCH_2CH_2CN + HCHO$$

$$\Big\downarrow \text{2 steps}$$

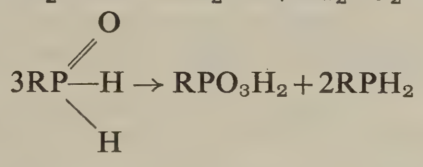
$$P(CH_2CH_2CN)_3 + 2CH_2O$$

Phosphorus analogues of Mannich bases are obtained by the action of primary and secondary amines on phosphonium salts which contain at least two hydroxymethyl groups,[280] and by other routes indicated below[280–2, 2178]:



Phosphonous acids and their salts undergo an oxidation–reduction reaction at temperatures in the range 100°–250° giving primary phosphine and phosphonic acid[83, 283]; secondary phosphine oxides (phosphinous acids) behave similarly when heated alone above 200°[282] or in the presence of sodium hydroxide[284]; primary phosphine oxides generally undergo oxidation–reduction in the pure state at or just above room temperature[1909]:

$$3PhPO_2H_2 \rightarrow PhPH_2 + 2PhPO_3H_2$$
$$2Bu_2POH \rightarrow Bu_2PH + Bu_2PO_2H$$



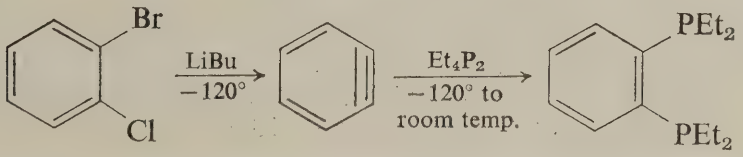
$$3RP(=O)(H)\text{—}H \rightarrow RPO_3H_2 + 2RPH_2$$

MISCELLANEOUS ROUTES TO PHOSPHINES

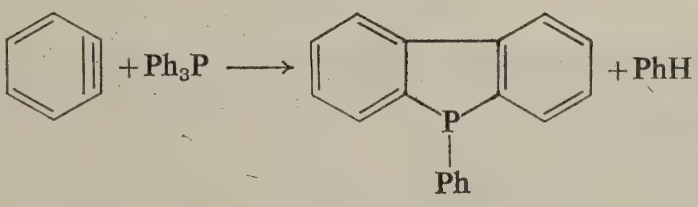
Mixtures of primary, secondary, and tertiary phosphines, and phosphonium salts, are obtained by heating phosphonium iodide with alkyl halides and zinc or zinc oxide.[240, 17, 38, 134, 250, 1740] Addition of water to the reaction mixture liberates any unreacted phosphine and primary alkylphosphine from their salts; the secondary[242] and tertiary phosphines are liberated by adding alkali or ammonia. Small amounts of tertiary phosphines are formed by heating the $PH_4I$ with alcohols.[1746] For reactions of carbonyl compounds which yield phosphines, see p. 929.

Tetra-alkyldiphosphines add across the carbon–carbon bond in unsaturated compounds such as ethylene and benzyne. The preparation of tetramethylethylenediphosphine[296] and *o*-phenylene-bis(diethylphosphine)[155] is indicated below:

$$Me_2P\text{—}PMe_2 + C_2H_4 \xrightarrow{\Delta} Me_2PCH_2CH_2PMe_2$$



Benzyne reacts with triphenylphosphine giving up to a 40% yield of 9-phenyl-9-phosphafluorene[298–9]:



Activated aromatic compounds such as *N,N*-dialkylanilines react with $PCl_3$ in the presence of bases such as pyridine and under reflux to form tertiary dialkylaminoarylphosphines as end products[230]:

$$3PhNR_2 + PCl_3 \longrightarrow (R_2NC_6H_4)_3P \qquad (R = Me, Et)$$

With zinc chloride as catalyst 1,3,5-trimethoxybenzene and phosphorus trichloride form tris(2,4,6-trimethoxyphenyl)phosphine in about 80% yield even when a large excess of $PCl_3$ is used.[99]

Phosphine and aroyl chlorides condense in the presence of pyridine giving trisaroylphosphines[300, 839]:

$$PH_3 + 3ArCOCl \rightarrow (ArCO)_3P \qquad (Ar = C_6H_5,\ p\text{-}CH_3.C_6H_4,\ \alpha\text{- and }\beta\text{-naphthyl}).$$

Condensation of phosphines with organometallic halides of lead[1741] or tin[1737] in the presence of a tertiary amine or the use of a metal phosphide in liquid ammonia[233] gives tertiary phosphine compounds having a phosphorus–metal bond:

$$Ph_3PbCl + Ph_2PH \xrightarrow{R_3N} Ph_3Pb{-}PPh_2$$
$$R_nSnX_{(4-n)} + (4{-}n)Ph_2PH \xrightarrow{R_3N} R_nSn(PPh_2)_{4-n} \qquad (n = 1, 2, 3)$$
$$Ph_2PNa + R_3SnX \xrightarrow{NH_3\,(1)} Ph_2P{-}SnR_3$$

Primary phosphines can be prepared by treating the $PH_3,AlCl_3$ complex with alkyl chlorides or bromides followed by hydrolysis with cold water[293-4]:

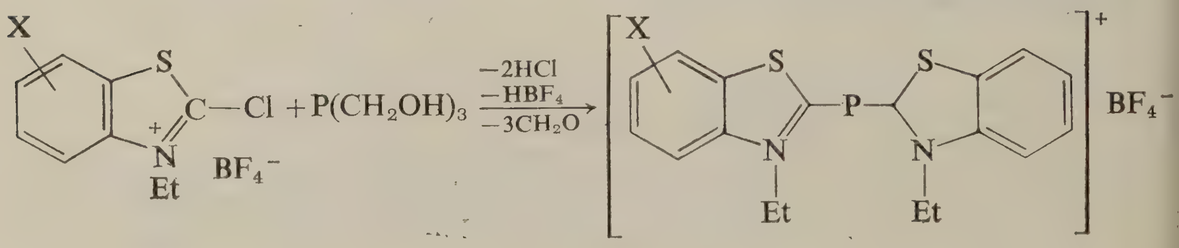
$$AlCl_3 + PH_3 \rightarrow PH_3,AlCl_3 \xrightarrow{RCl} RPH_3.AlCl_4 \xrightarrow{H_2O} RPH_2 + HAlCl_4 \text{ hydrate}$$

The phosphorus analogue of hydrocyanic acid, HCP, can be obtained as a very reactive colourless gas by passing phosphine through a low intensity rotating arc struck between graphite electrodes in a water-cooled copper reactor.[301] It is stable to storage in the pure state only at temperatures below its triple point, −124·2°C.; reaction with hydrogen chloride at −110°C. gives methylphosphonous dichloride.

Phosphines having the structure $>PCH_2X$ (where $X = PPh_2$, SR, OAr) may be obtained by condensation of dialkylaminomethylphosphines with compounds containing an active hydrogen atom such as mercaptans, phenols, ethylacetoacetate and diphenylphosphine:

$$P(CH_2NEt_2)_3 + 3RSH \xrightarrow{\Delta} P(CH_2SR)_3 + 3Et_2NH \,^{282}$$
$$R_2PCH_2NEt_2 + Ph_2PH \xrightarrow{\Delta} R_2PCH_2PPh_2 \,^{2319-20}$$

A new class of highly coloured phosphorus compounds termed 'phosphamethine cyanines', containing a tervalent phosphorus atom having a co-ordination number of 2, are formed by condensation of trishydroxymethylphosphine with 2-chloro-*N*-ethyl benzthiazolium fluoroborate in dimethyl formamide solution with a base.[2321] The crystal structure of bis[*N*-ethyl-benzthiazole-(2)] phosphamethine-cyanine perchlorate[2322] shows a C–P–C bond angle of 104·6° and both P–C bond lengths 1·76 Å.

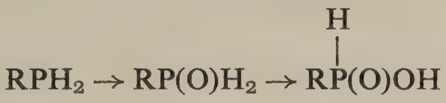


## Reactions of Phosphines

### OXIDATION

All phosphines are readily subject to oxidation. Primary, secondary and tertiary alkylphosphines are generally oxidized by atmospheric oxygen; tertiary arylphosphines are, in general, more stable to atmospheric oxygen but undergo oxidation at elevated temperatures with a wide variety of oxidizing agents.

Oxidation of monoalkylphosphines by air or oxygen is said to yield the corresponding phosphonic acid, phosphonous acid and orthophosphoric acid in a ratio of 3 : 6 : 1 which is independent of the temperature or oxygen concentration.[101] Under controlled conditions primary phosphines are oxidized by hydrogen peroxide, *tert*-butyl peroxide or nitrogen dioxide to monoalkylphosphine oxides[102–3]; more vigorous oxidation by the first reagent gives largely the phosphonous acid[145]:



$$RPH_2 \rightarrow RP(O)H_2 \rightarrow R\overset{H}{P}(O)OH$$

Secondary phosphines are oxidized by air[104–5] or oxygen[106] under controlled conditions to secondary phosphine oxides; more vigorous oxidation with air[170] or nitric acid[147,169] gives phosphinic acids:

$$R_2PH \rightarrow R_2P(O)H \rightarrow R_2PO_2H$$

The reactivity of tertiary phosphines, $R_3P$, towards oxygen decreases as

$$R = \text{benzyl} > \text{alkyl} > \text{aryl}^{107}.$$

Oxidation of trialkylphosphines is a relatively long chain free-radical process,[108] the major products being trialkylphosphine oxide, alkyldialkyl phosphinate, dialkylalkyl phosphonate and trialkyl phosphate[107]; oxidation of tributylphosphine in hexane solution by oxygen gives $R_3PO$, $R_2PO.OR$, $RPO.(OR)_2$, and $(RO)_3PO$ in the molar ratios 42 : 49 : 6 : 3 respectively. Triphenylphosphine is not oxidized by air in benzene solution at 80° but undergoes ready oxidation under these conditions in the presence of a free-radical initiator.[107]

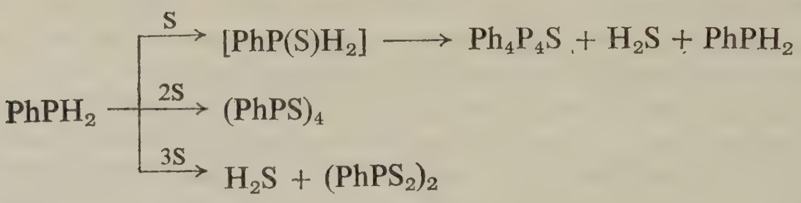
Tertiary alkyl/arylphosphines are readily oxidized by several reagents: aqueous $H_2O_2$[31,88,104,318]; ozone[130]; oxides of nitrogen such as $N_2O$,[110] NO[111–2] and $N_2O_4$[113,118]; other inorganic oxidizing agents such as $Na_2O_2$,[87] $CrO_3$,[1921] $KClO_3$,[228] HgO,[283] $FeCl_3$,[1742] $HNO_3$,[273–4,1939] $SO_2$ with $PBr_3$ or $POBr_3$ catalyst,[1681], $SeO_2$,[1854] $MnO_2$[1994]; a wide variety of organic oxidizing agents such as alkylhydroperoxides, peracids, alkylhydrochlorites or peresters[114–29]:

$$R_3P \xrightarrow{[0]} R_3PO$$

The stereochemistry of the oxidation of optically active phenylmethylpropylphosphine by percompounds such as $Me_3COOH$, $Me_3COCl$, and $Me_3CCO_3Me$, has been reported.[114] Sulphur trioxide forms in Freon solution at −78° 1 : 1 adducts with $PhPH_2$, $Ph_2PH$, $Ph_3P$, $Ph_2PCl$ and $PhPCl_2$; oxidation occurs at room temperature. The adduct $Ph_2PH,SO_3$ undergoes rearrangement in polar solvents giving $Ph_2P–SO_3H$, obtained also from $Ph_2PH$ and $ClSO_3H$.[109]

### REACTIONS WITH SULPHUR, SELENIUM AND TELLURIUM

Sulphur reacts with primary phosphines giving ill-defined products.[1] The nature of the products obtained from phenylphosphine and sulphur, reported to be $PhPH_2S$ and $Ph_3P_3S_2$,[1] has been clarified by Maier.[133] With a 1 : 1 molar ratio of $PhPH_2 : S$ the product is phenylphosphine sulphide, $PhP(S)H_2$, which is unstable and decomposes to a mixture of tetraphenyl*cyclo*tetraphosphine monosulphide, hydrogen sulphide and monophenylphosphine; a 1 : 2 ratio gives tetraphenyl*cyclo*tetraphosphine tetrasulphide $(PhPS)_4$; a 1 : 3 ratio gives an almost quantitative yield of *trans* dimeric phenylthionophosphine sulphide $(PhPS_2)_2$:



$$\begin{aligned} PhPH_2 &\xrightarrow{S} [PhP(S)H_2] \longrightarrow Ph_4P_4S + H_2S + PhPH_2 \\ PhPH_2 &\xrightarrow{2S} (PhPS)_4 \\ PhPH_2 &\xrightarrow{3S} H_2S + (PhPS_2)_2 \end{aligned}$$

In contrast with phenylphosphine, alkylphosphines yield only one product, tetraalkyl *cyclo*tetraphosphine tetrasulphide, on reaction with sulphur[2187]:

$$RPH_2 + S \rightarrow (RPS)_4 \sim 80\% \qquad (R = n\text{-butyl}, n\text{-octyl})$$

Reaction of phenylphosphine with selenium in benzene solution under reflux afforded tetraphenyl *cyclo*tetraphosphine tetraselenide in 80% yield.[2187] Secondary phosphines are oxidized by sulphur under controlled conditions giving successively secondary phosphine sulphides, $R_2P(S)H$,[66, 131, 1747] and phosphinodithioic acids, $R_2PS_2H$.[66] With an excess of sulphur, phosphinic acid derivatives, $[R_2PS]_2S_3$ and $[R_2PS]_2S$, are formed[134]; these, on treatment with basic aqueous reagents, give salts of phosphinodithioic acids[1, 134, 141] which are also formed by the action of sulphur and aqueous ammonia[585]:

$$R_2PH + 2S + NH_4OH \rightarrow R_2PS_2^- NH_4^+$$

Several secondary phosphines have been shown to react with selenium in benzene solution to form the secondary phosphine selenide $R_2P(Se)H$.[2177] Tertiary phosphines readily add sulphur giving the corresponding tertiary phosphine sulphides.[1, 200] Kinetics of the reaction of triarylphosphines with sulphur have been studied[132, 135-7] and the results to 1961 reviewed by Cadogan.[355] Selenium[1, 138, 141, 200] and tellurium[140, 2349] add to $R_3P$ less readily than does sulphur to form the corresponding selenide, $R_3PSe$, and telluride, $R_3PTe$, respectively.

### HALOGENATION

Primary and secondary phosphines react vigorously with halogens. Unless special precautions are taken the compounds are decomposed. Under controlled conditions halogenation yields halogenophosphines[142, 163] ($RPX_2$, phosphonous dihalide; $R_2PX$, phosphinous halide) which on further halogenation yield halogenophosphoranes[163]:

$$\begin{aligned} RPH_2 + 2X_2 &\rightarrow RPX_2 + 2HX \\ RPX_2 + X_2 &\rightarrow RPX_4 \qquad (X = Cl, Br, I) \end{aligned}$$

Chlorophosphines are best prepared from phosphines by halogenation using phosgene[143, 333, 534]:

$$R_nPH_{(3-n)} \xrightarrow{COCl_2} R_nPCl_{(3-n)} \qquad (n = 1 \text{ or } 2)$$

Tertiary phosphines readily add halogens forming dihalogenophosphoranes, $R_3PX_2$ ($X = Cl, Br, I$). Phenylphosphine and thionyl chloride react to give 20–30% $(PhPSO)_3$ and higher polymers.[171] Diphenylphosphine is readily converted to diphenylbromophosphine using *N*-bromosuccinimide.[289]

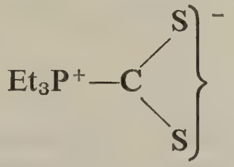
COMPLEXES WITH ORGANIC COMPOUNDS

Tertiary phosphines form adducts with many unsaturated compounds, particularly those having cumulative unsaturation. The adducts are generally solids and are frequently highly coloured. The structure of such adducts has been the subject of much hypothesis and discussion in the literature (cf. ref. 117); recent work has done much to clarify the situation.[173, 182–3, 192–3] Many of the adducts have the character of phosphonium zwitter-ions and react with alkyl halides or inorganic acids to form normal phosphonium salts[14, 180, 182–3, 190]:

$$R_3P + X{=}Y \rightarrow R_3\overset{+}{P}{-}X{-}Y^- \xrightarrow{MeI} R_3\overset{+}{P}{-}X{-}Y{-}MeI^-$$

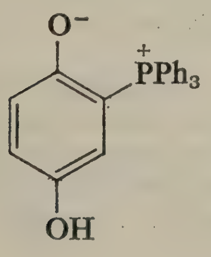
Tertiary phosphine adducts are reported with carbon disulphide,[139, 172–5, 190] carbon diselenide,[191] aryl isothiocyanates,[139, 176, 202] alkyl and aryl azides,[110] aliphatic diazo compounds,[110, 179, 180] diphenyl ketene,[177] ethylene-1 : 2-dicarbonyl compounds such as maleic anhydride,[181, 192, 195] and dibenzoylethylene, acetylene-1,2-dicarbonyl compounds such as dibenzoyldiacetylene and esters of acetylenedicarboxylic acid,[183, 193] highly polarized olefins, e.g., benzalmalonic esters and substituted benzalmalononitrile and vinylidene dicyanide[180] and 2-benzal-1,3-diketohydrindene,[180] aromatic compounds such as quinones,[139, 180–3, 186, 188] azlactones,[117, 180] triphenylmethane dyestuffs[187] and *o*-dinitrobenzene.[180]

The red, crystalline adduct of triethylphosphine with carbon disulphide, $Et_3P,CS_2$, was reported by Hoffmann in 1861[14]; many trialkylphosphines form similar red complexes but triphenylphosphine and trivinylphosphine give no colour with carbon disulphide.[210] *X*-Ray diffraction of the $Et_3P,CS_2$ complex has established the presence of a bond between the phosphorus atom and the carbon atom of the $CS_2$[173]; the shape of the molecule corresponds to that of a zwitter-ion of a quaternary phosphonium derivative of a dithioformate, i.e.,

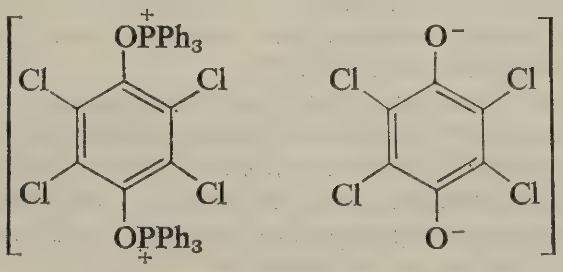


as proposed by Jensen.[172] The infra-red spectra and dipole moments of a number of tertiary phosphine–$CS_2$ adducts support a similar structure.[190, 2315] Carbon diselenide adducts of $Me_3P$ and $Et_3P$ are green; their infra-red spectra support the structure $R_3P^+{-}CSe_2^-$.[191]

*p*-Benzoquinone and triphenylphosphine form a 1 : 1 adduct in which phosphorus is attached to a carbon atom of the benzene ring **XIX**; chloranil gives an adduct with a 1 : 1 molar ratio but having a P–O–C bond (XX).[182–3, 186] The difference has been attributed to the resistance of chloranil to nuclear substitution and to its higher oxidation–reduction potential.[182]

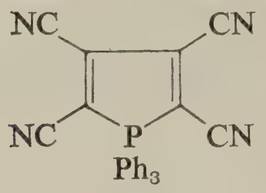


**XIX**

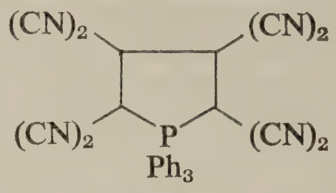


**XX**

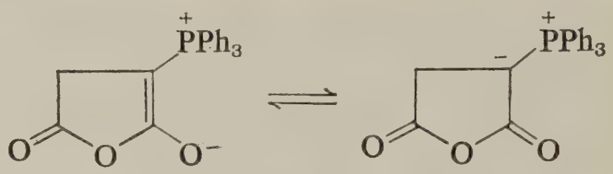
Triphenylphosphine combines with dicyanoacetylene and tetracyanoethylene to give tetracyano-*P*,*P*,*P*-triphenylphosphole (**XXI**) and octacyano-*P*,*P*,*P*-triphenylphospholidine (**XXII**) respectively.[184] With maleic anhydride the adduct has been shown by nuclear magnetic resonance and infra-red spectroscopy and by direct synthesis from chlorosuccinic anhydride to be anhydrosuccinylidine triphenyl phosphorane **XXIII**.[192]



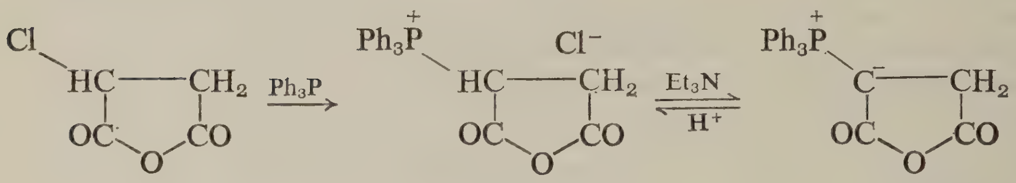
**XXI**



**XXII**

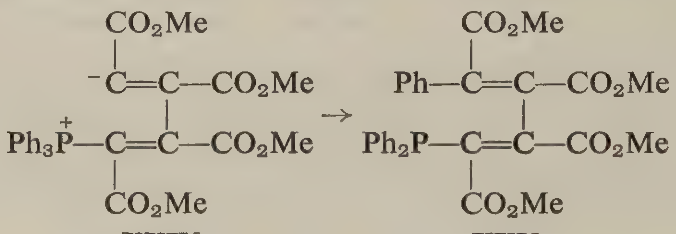


**XXIII**



i.e. **XXIII**

Triphenylphosphine forms a number of adducts with dimethyl acetylenedicarboxylate; at −50°C. an adduct formulated **XXIV** is formed, which rearranges at room temperature to **XXV**. This is the product obtained when the reaction is conducted in boiling ether[193]:



$$Ph_3\overset{+}{P}-C(CO_2Me)=C(CO_2Me)-C(CO_2Me)=\overset{-}{C}(CO_2Me) \rightarrow Ph_2P-C(CO_2Me)=C(CO_2Me)-C(CO_2Me)=C(CO_2Me)-Ph$$

**XXIV** **XXV**

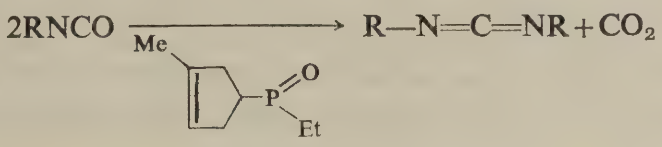
Thermodynamic parameters for the formation of adducts ArCH($\overset{+}{P}Bu_3$)–$\overset{-}{C}(CN)_2$ from tri-*n*-butylphosphine and seven arylmethylenemalononitriles in methanol solution have been evaluated.[582]

Adducts of tertiary phosphines with aliphatic diazo compounds (except with 9-diazofluorene[189]) and azides, phosphazines ($R_3P{=}N{-}N{=}CR_2$) and phosphazides ($R_3P{=}N{-}N{=}NR$) respectively, decompose on heating. The former give methylenephosphorane derivatives and the latter iminophosphoranes.[110,177,179,189,198]

The reaction of triphenylphosphine with aryldiazonium salts in aqueous solution proceeds according to the equation[1995-6]:

$$Ph_3P + ArN_2^+X^- \rightarrow [Ph_3\overset{+}{P}{-}N{=}NArX^-] \xrightarrow{Ph_3P} Ph_3\overset{+}{P}NHNHArX^- + Ph_3PO$$

Olefins of the type $CH_2{=}CHX$, where X is powerful electron acceptor ($CO_2R$, CHO, OAc, $NO_2$) are polymerized by tertiary phosphines to compounds of the type $R_3\overset{+}{P}CH_2(CHX\text{–}CH_2)_nCH^-X$[199]; the tertiary alkylphosphine catalysis of the polymerization of acrylonitrile is reported.[204, 209, 235] Isocyanates such as PhNCO can be polymerized to trimers by the addition of small amounts of tertiary phosphines.[180] A more important reaction is the formation of carbodi-imides by heating isocyanates with catalytic amounts of phosphines, particularly phosphorus-substituted phospholines or phosphorus-substituted phospholidines[236] or their corresponding oxides[237] (see phosphine oxides), e.g.,



$$2RNCO \longrightarrow R\text{—}N{=}C{=}NR+CO_2$$

PHOSPHINE COMPLEXES WITH INORGANIC COMPOUNDS

The ability of phosphines to form co-ordination compounds with metal salts has been known for over a century. Cahours and Hofmann in 1857 recorded the formation of a red complex salt of $Et_3P$ and $PtCl_4$[141] and later obtained similar complexes with $EtPH_2$[169] and $Et_2PH$.[1738] The formation of a zinc iodide complex of $Et_3P$ was noted by Cahours in 1862.[138] Co-ordination compounds are formed with many metal salts; these generally have characteristic melting points and may be used to characterize individual phosphines; many of the complexes, particularly those with the transition metals, are highly coloured.

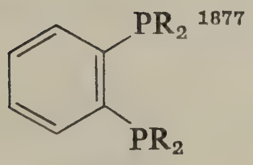
More recently the ability of trivalent phosphorus compounds to form strong $p\pi\text{–}d\pi$ bonds to metals[1804, 1861] together with increased interest in the chemistry of co-ordination compounds in connection with problems in inorganic stereochemistry, the nature of the co-ordinate bond, the stabilization of valency states, and particularly the development of certain of the compounds as catalysts, has resulted in a rapid development of the use of tertiary phosphine ligands. The need for suitable phosphine ligands, particularly di- and polydentate ligands, has contributed in no small way to the development of synthetic methods for ditertiary phosphines such as **XXVI**, **XXVII** and **XXVIII**, tritertiary phosphines **XXIX** and **XXX** and tetratertiary phosphines **XXXI** and **XXXII**.

$CH_2(PR_2)_2$[1816]

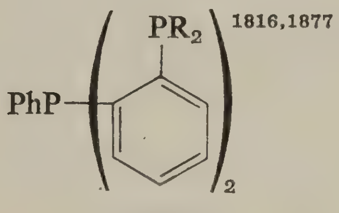
**XXVI**

$R_2PCH_2CH_2PR_2$[1816,65]

**XXVII**



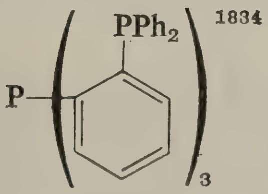
**XXVIII**



**XXIX**

$MeC(CH_2PPh_2)_3$[1816]

**XXX**



**XXXI**

$C(CH_2PPh_2)_4$[2323]

**XXXII**

Co-ordination compounds containing polydentate phosphorus ligands are reviewed by Venanzi.[1833]

### TERTIARY PHOSPHINE–METAL SALT COMPLEXES

With simple tertiary phosphines univalent copper[1750, 1754, 1758] and silver[1751, 1754] form fourfold macromolecular 1 : 1 co-ordination compounds such as $(R_3P,MI)_4$ ($M = Cu^+, Ag^+$), 2 : 1 adducts such as $[(PhPMe_2)_2,MI]$,[1754] 3 : 1 complexes $(R_3P)_3MX$ ($R_3P$ = 2-phenyl*iso*phosphindoline)[1758] and 4 : 1 adducts $[(R_3P)_4,MClO_4]$.[1756, 1758] The most frequently prepared gold(I) complexes are linear 1 : 1 complexes $[R_3P,AuX]$ ($X = Cl, Br, I$)[1751, 1852]; 2 : 1 and 3 : 1 complexes are formed with 2-phenyl*iso*phosphindoline.[1758] The 1 : 1 complexes react with halogens giving auric complexes, $R_3P,AuCl_3$.[1752] The *X*-ray crystal analysis of $Et_3P,AuBr_3$ shows a planar 4-co-ordinate gold(III) atom.[1761] The reaction of $Ph_3P,AuCl$ with sodium salts of metal carbonyls of iron, cobalt or manganese gives triphenylphosphine–gold metal carbonyls, e.g.,

$$Ph_3P,AuCl + NaMn(CO)_5 \rightarrow Ph_3PAu{-}Mn(CO)_5\ ^{1757}$$

Complexes of Cu(I) and Ag(I) with chelating ditertiary phosphines such as *P,P,P′,P′*,-tetraethylethylene-1,2-diphosphine contain a 4-co-ordinate chelated metal cation $[CuL_2]^+[CuLX_2]^-$, $[AgL_2][AgI_2]$ ($L = Et_2PCH_2CH_2PEt_2$; X = halogen). AuI forms the diphosphine-bridged complex $IAu,P(Et_2)CH_2CH_2P(Et_2),AuI$ which reacts with iodine to form the Au(III) bridged complex $I_3Au,Et_2PCH_2CH_2PEt_2,AuI$.[56] Compounds such as 4-methyltetraethyl-*o*-phenylenediphosphine form 4-co-ordinate Au(I) complex salts such as $[AuL_2]I$, and Au(III) complexes such as $[LAuI]X_2$ ($X = I, ClO_4$).[1762]

Zinc,[1754, 1784] cadmium[1754, 1763] and mercuric[1752, 1754] halides form 2 : 1 addition compounds $(R_3P)_2,MX_2$ with tertiary phosphines. Compounds which have a halogen-bridged structure having a higher ratio of metal halide to tertiary phosphine are formed from Cd(II) and Hg(II) halides, e.g., $[(R_3P,MX_2)_2]$, $[(R_3P)_3,(MX_2)_2]$ (M = Cd or Hg); and $[(R_3P)_2(HgX_2)_3]$, $[(R_3P)_2(HgX_2)_4]$. Tetraethylethylenediphosphine forms complexes of the type $ML_2X_2$ (M = Zn, Cd, Hg).[56]

Addition compounds of tertiary phosphines with halides and organometallic derivatives of the Group III metals are reviewed by Stone.[1776–7]

Silicon halides form tertiary phosphine complexes $[SiX_4,(PR_3)_2]$ (X = F, Cl, Br) which are non-electrolytes, and which dissociate to their constituents on being heated.[1782] Tertiary phosphine complexes of germanium iodide, $R_3P,GeI_2$,[1783] stannic halides, $(R_3P)_2,SnX_4$ (X = Cl, Br)[1784–5] and Pb(II) bromide, $PbL_2Br_2$ ($L = Et_2PCH_2CH_2PEt_2$),[56] are reported. Titanium(III) and titanium(IV) complexes $TiCl_3,(R_3P)_2$ and $TiCl_4,R_3P$ (R = Et, Ph) have been isolated.[1853]

Phosphine complex salts analogous to Reinecke salts, $Et_3\overset{+}{P}HCr(SCN)_4(R_3P)_2^-$, are obtained by treating *iso*-propanol solutions of $K_3Cr(SCN)_6$ with trialkylphosphine and then hydrochloric acid.[1841] Analogous compounds are formed with tetraethyl- or tetra*cyclo*hexyl-ethylenediphosphine:

$$[R_2\overset{+}{P}H{-}CH_2CH_2\overset{+}{P}HR_2][Cr(SCN)_4R_2P{-}CH_2CH_2PR_2]_2^{-\ 1787};$$

$Ph_3P$, $Ph_2PCH_2CH_2PPh_2$ and $(Ph_2P)_2CH_2$ do not react.

Vanadium trichloride and tertiary alkylphosphines react to give complexes such as $VCl_3,(PR_3)_2$, but triphenylphosphine and tri(*cyclo*hexyl)phosphine form complexes of variable composition.[1837]

Although uranium(IV) halide complexes $(R_3P)_2,UX_4$ (X = Cl, Br) have been reported by Allison and Mann,[1785] in a recent investigation Gans and Smith[1786] found no evidence for such compounds. They show that in ethanol, tetrahydrofuran or acetonitrile solutions the compounds formed are diphosphonium tetrahalogenodioxouranates $(R_3\overset{+}{P}H)_2(UO_2Cl_4)^{2-}$.

Purple red[1792] and yellow[1791] triphenylphosphine rhenium chloride complexes formulated as $ReCl_3,(Ph_3P)_2$ have recently been shown to be $ReOCl_3,(Ph_3P)_2$ and $ReCl_3,(Ph_3PO)_2$ respectively.[1760] Rhenium(II), rhenium(III), rhenium(IV) and rhenium(V)–tertiary phosphine complexes, $ReX_2(PPh_3)_2$ ($X = Cl$, I), $(ReCl_3,Ph_3P)_n$, $ReX_4,(PR_3)_2$ ($X = Cl$, Br, I), and $ReOX_3,(R_3P)_2$ respectively, are reported.[1788–90, 1880] The crystal structure of $(ReCl_3,PhPEt_2)_n$ shows it to be a trimer, i.e. tris(diethylphenylphosphine)nonachlorotrirhenium.[1851]

Numerous tertiary phosphine transition metal salt complexes have been prepared, particularly from nickel, cobalt, platinum and palladium salts. The most frequently reported cobalt and nickel complexes are Ni(II)[88, 1765, 1767, 1769, 1770, 1772–3, 1793, 1857] and Co(II)[88, 172, 1767, 1856] compounds of the type $(R_3P)_2MX_2$ ($M = Co$, Ni; $X = Cl$, Br, I, CN, CNS, $NO_2$, $NO_3$, CNO) which are generally prepared by the direct reactions:

$$MX_2 + 2R_3P \rightarrow (R_3P)_2MX_2 \quad \text{or} \quad (R_3P)_2MX_2 + 2X'^- \rightarrow (R_3P)_2MX'_2 + 2X^-$$

The cyanate complexes are prepared by the reaction:

$$M(CNO)_4^{2-} + 2R_3P \rightarrow (R_3P)_2M(NCO)_2 + 2NCO^- \qquad (M = Ni(II),\ Pd(II),\ Pt(II))$$

An *X*-ray study of the Ni(II) complexes shows a pseudo-tetrahedral structure about the Ni atom.[1773]

Pyramidal derivatives of nickel(III) and cobalt(III), $(R_3P)_2MX_3$ ($X = Cl$, Br), have been obtained by treating the appropriate Ni(II) or Co(II) halide complex with bromine or a nitrosyl halide.[1766–8] Salts of triphenylphosphine-coordinated Ni(II) anions such as $M^+[Ph_3P.NiX]$ ($M = Et_4N^+$, $Ph_4P^+$; $X = Br$, I) are recorded.[1777]

Platinous and palladous halides form planar 2:1, $(R_3P)_2,MX_2$, and dimeric halogen bridged 1:1, $[R_3PM(X)X_2M(X)PR_3]$, complexes with tertiary phosphines.[172, 1753, 1763, 1765, 1774–5, 1856] The platinum compounds can be isolated as *cis* and *trans* isomeric forms. Tertiary phosphines having a pent-4-enyl substituent form platinum(II) complexes of the type $R_3P,PtX_2$ ($X = Cl$, Br, I) in which a C═C bond and the phosphorus atom are co-ordinated to the platinum; the analogous palladium(II) complexes are dimeric and the C═C bond is not co-ordinated to the Pd atom.[1858]

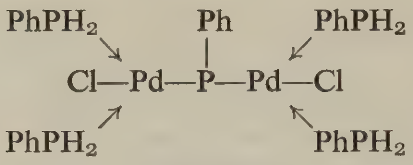
Ruthenium(II) and osmium(II)–tertiary phosphine complexes of the type $M_2Cl_3(PR_3)_6Cl$ ($M = Ru$, Os; $R_3P = PhPEt_2$, $PhPMe_2$) and *cis-trans* octahedral ditertiary phosphine complexes $[MX_2(\text{chelate})_2]$ ($M = Ru$, Os; X = halogen, SCN; chelate $= C_2H_4(PR_2)_2$, $CH_2(PPh_2)_2$, *o*-$C_6H_4(PEt_2)_2$) are reported.[1836] Ruthenium(III) forms monomeric complexes, e.g., $RhX_3,(PR_3)_3$ ($X = Cl$, Br) and two types of binuclear halogen-bridged complexes.[1835]

2-Phenyl*iso*phosphindole complexes with Ni(II), Pt(II) and Pd(II)[1760] and Co(II)[1759] halides to give unusual 5-coordinated compounds, $(R_3P)_3,MX_2$, in addition to the normal complexes $(R_3P)_2,MX_2$. Rh(III) halides give normal 6-coordinated Rh(III) complexes $(R_3P)_3RhX_3$, Ir(III) halides form complexes of the type $(R_3P)_3IrHX_2$ and $(R_3P)_3IrX_3$.[1759] Tetraethylethylenediphosphine forms the following nickel(II), nickel(III), and cobalt(II) complexes: $NiBr_2,L$, $NiBr_3,L$, $NiX_2,L_2$ ($X = ClO_4$, Br), $CoX_2,L$ ($X = Br$, I), $CoX_2,L_2$ ($X = Cl$, Br, I). Tris-(*o*-diphenylphosphinophenyl)phosphine (QP) complexes of the types $[MX(QP)]^+X^-$ ($M = Fe(II)$, Co(II), Ni(II), Pt(II); $X = ClO_4$, $Ph_4B$), and [Co(I)X(QP)] are described by Venanzi and co-workers.[1883–4]

### PRIMARY AND SECONDARY PHOSPHINE–METAL HALIDE COMPLEXES

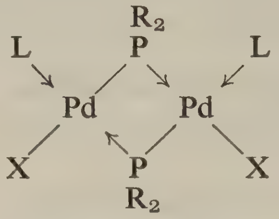
Complexes of primary and secondary phosphines with metal salts have been less extensively studied than those of tertiary phosphines. Complexes of phenylphosphine,[1839] diphenylphosphine,[1842] *cyclo*hexylphosphine[1840] di*cyclo*hexylphosphine[1838] and diethylphosphine[1838] with Cu(I), Cr(III), Fe, Co, Ni and Pd halides, are described by Issleib and co-workers; examples are, $(PhPH_2,CuCl)_4$, $(RPH_2)_2,MX_2$ (R = *cyclo*hexyl; $M = Co$, Ni, Fe); $(R_2PH)_2,MX_2$ ($R = Et$, Cy; $M = Co$, Fe);

$(R_2PH)_4,MX_2$ (M = Co, Ni; R = Et, Cy); $[PdCl(PPh_2),Ph_2PH]$; $CrCl_3L_3$ (L = $PhPH_2$, $Et_2PH$); and the phosphorus-bridged palladium compound **XXXIII**:



**XXXIII**

Novel phosphorus-bridged palladium compounds, **XXXIV**,



**XXXIV**

have been obtained by Hayter by treating complexes of the type $PdX_2,LL'$ (X = halogen, L = $R_2PH$, L′ = $R_2PH$ or $R_3P$) with an amine base,[1843–5,1849] e.g.

$$2PdCl_2(Et_2PH)_2 \xrightarrow[-B,HCl]{B} [PdClR_2P.R_2PH]_2 \qquad (R = Et, Ph)$$

The ruthenium complex $RhCl_3,(Me_2PH)_3$ does not form a bridged complex on treatment with a base.[1849] The chemistry of phosphorus-bridged complexes of transition metals has been reviewed.[2188]

### TERTIARY PHOSPHINE COMPLEXES HAVING FORMALLY ZEROVALENT METAL

A number of tertiary phosphine–metal complexes have been made in which the metal exhibits a formal valency of zero. Tetraethyl-*o*-phenylenediphosphine dissolves cobalt and palladium at about 200° giving the complexes $[M(o\text{-}C_6H_4(PEt_2)_2)_2]$ (M = Co, Pd); iron, ruthenium, rhodium and platinum do not react but iron, in the presence of hydrogen, gives a *trans* dihydro complex $[FeH_2,o\text{-}C_6H_4(PEt_2)_2]$.[1827] Tetraphenylethylenediphosphine dissolves Raney nickel at about 160° giving $Ni[C_2H_4(PPh_2)_2]_2$.[1796] Various methods have been used to prepare phosphine complexes of other zerovalent metals. Octahedral $M[C_2H_4(PMe_2)_2]_3$ (M = V, Cr, Mo, W),[1829] tetrahedral $M[C_2H_4(PMe_2)_2]_2$ (M = Fe, Co),[1829] and other complexes of the type $ML_2$ (M = Ni, Pd; L = $C_2H_4(PMe_2)_2$, $MeC(CH_2PPh_2)_3$),[1830] have been obtained by reduction of higher valent complexes. Zerovalent phosphine molybdenum compounds can be obtained by heating dibenzenemolybdenum with three equivalents of $C_2H_4(PMe_2)_2$ or $o\text{-}C_6H_4(PR_2)_2$ (R = Et, Ph).[1828] Triphenylphosphine–platinum complexes, $Pt(PPh_3)_4$ and $Pt(PPh_3)_3$, are reported by Malatesta.[1797,1832] They react with carbon monoxide eliminating one equivalent of $Ph_3P$ to give the complexes $PtCO(PPh_3)_3$ and $PtCO(PPh_3)_2$ respectively.

Reppe and Sweckendiek[1793] showed that triphenylphosphine and tributylphosphine would react with metal (Fe, Ni, Co) carbonyls, replacing one or two of the carbon monoxide ligands to form tertiary phosphine–metal carbonyl complexes such as $Ph_3P,Ni(CO)_3$, $(Bu_3P)_2,Ni(CO)_2$, $(Ph_3P)_2,Fe(CO)_3$, $Ph_3P,Co(CO)_3$. More recent work has resulted in the isolation of tertiary phosphine–metal carbonyl complexes from the following metals, Cr,[1794,1815] Mo,[1794,1815] W,[1794,1815] Fe,[1793,1800] Co,[1793,1809] Ni,[1793,1795,1804] Mn,[1745,1798,1810–1] Pt[1797] and V.[1808] Tertiary phosphine–manganese carbonyl salts $[Mn(CO)_4,PR_3]^-M^+$ (R = Et, Ph; M = Na, Li) are prepared by reduction of the corresponding dimeric carbonyls $[Mn(CO)_4,PR_3]_2$ with metal amalgams.[1811] Tertiary phosphine manganese carbonyl halides,[1811–2,1860] hydride,[1811] and methyl[1811] [$XMn(CO)_3,PR_3$] ($X = Cl, H, CH_3$) are described. Acylcobalttricarbonyl–triphenylphosphine complexes can be prepared by the reaction of $Ph_3P$ with $RCo(CO)_4$ or with $NaCo(CO)_4$ and alkyl halide[1813-4]; they react with trimethyl phosphite to eliminate first one carbon monoxide and then the triphenylphosphine ligand[1814, 1859]:

$$Ph_3P + RCo(CO)_4 \rightarrow RCO{-}Co(CO)_3,PPh_3$$

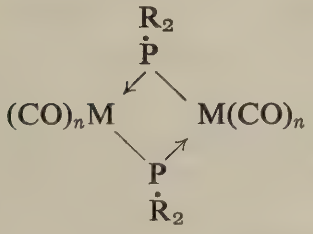
$$RCO{-}Co(CO)_3,PPh_3 \xrightarrow[-CO]{(MeO)_3P} RCO{-}Co(CO)_2,PPh_3,P(OMe)_3 \xrightarrow[-PPh_3]{(MeO)_3P} RCO{-}Co(CO)_2,(P(OMe)_3)_2$$

Rhenium pentacarbonyl chloride and $Ph_3P$ react to give $Re(CO)_4,PPh_3,Cl$.[1902]

Chelating ditertiary phosphines such as $(CF_3)_2PCH_2CH_2P(CF_3)_2$[1771] and [$C_2H_4(PR_2)_2$] ($R = Et$,[1796] $CH_2CH_2CN$[270]) react with nickel carbonyl displacing two carbon monoxide ligands to form the complexes $Ni(CO)_2$,(diphosphine); more powerful chelating ditertiary phosphines such as $C_2H_4(PPh_2)_2$ and [$o$-$C_6H_4(PR_2)_2$] ($R = Et, Ph$) replace all four carbon monoxide ligands giving Ni(diphosphine)$_2$ complexes.[1796] Ditertiary phosphines react with hexacarbonyls of chromium, molybdenun and tungsten to replace either 2 or 4 CO groups; tritertiary phosphines replace 3 CO groups.[1816]

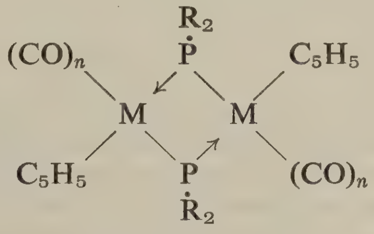
Tetrasubstituted diphosphines react with dimeric metal carbonyls of cobalt and manganese[1848] and with *cyclo*pentadienyl metal carbonyls of iron, nickel, molybdenum and tungsten,[1846-7] giving dimeric phosphorus-bridged complexes, **XXXV** and **XXXVI** respectively, e.g.,

$$Mn_2(CO)_{10} + R_2P{-}PR_2 \rightarrow [R_2P,Mn(CO)_4]_2 + 2CO$$



$M = Co$, $n = 3$
$M = Mn$, $n = 4$

**XXXV**



$M = Mo, W$; $n = 2$
$M = Fe$; $n = 1$
$M = Ni$; $n = 0$

**XXXVI**

The same complexes are obtained from phosphinous chlorides by the reactions:

$$2R_2PCl + 2NaMn(CO)_5 \rightarrow [R_2PMn(CO)_4]_2 + 2CO + 2NaCl^{1848}$$
$$2R_2PCl + 2Na[C_5H_5,Fe(CO)_2] \rightarrow [C_5H_5,Fe(PR_2)CO]_2 + 2CO + 2NaCl^{1847}$$

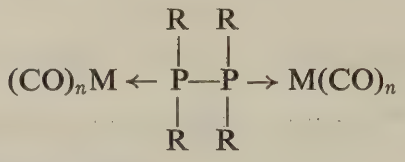
Vanadium compounds of structure **XXXV** ($R = Ph$ or/and H; $n = 4$) are obtained by treating vanadium hexacarbonyl with $PH_3$, $PhPH_2$ or $Ph_2PH$ in hexane solution[1808]:

$$2V(CO)_6 + 2PhPH_2 \rightarrow [V(CO)_4(PhPH)]_2 + 4CO + H_2$$

In the absence of solvent simple replacement of CO ligands occurs to give complexes such as $V(CO)_4(Ph_2PH)_2$.[1808]

Monomeric metal carbonyls of iron, chromium, nickel, molybdenum and tungsten[1795, 1850, 1862–4] react with tetrasubstituted diphosphines giving binuclear complexes, **XXXVII**, of the uncleaved diphosphine, e.g.,

$$2Cr(CO)_6 + R_4P_2 \rightarrow 2CO + [R_4P_2.Cr_2(CO)_{10}]$$



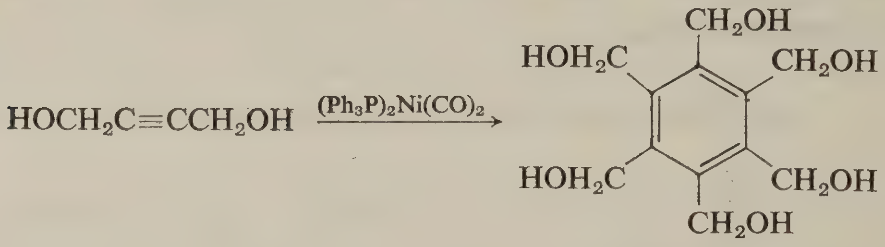
$$(CO)_nM \leftarrow \underset{R}{\overset{R}{P}}\text{—}\underset{R}{\overset{R}{P}} \rightarrow M(CO)_n$$

$M = Ni;\quad n = 3$
$M = Fe;\quad n = 4$
$M = Cr, Mo, W;\quad n = 5$

**XXXVII**

The Cr, Mn, and W complexes of $Me_4P_2$ undergo rearrangement on being heated, losing CO, to give complexes of type **XXXV**.[1863–4]

The polymerization of acetylenic compounds to benzene derivatives in the presence of tertiary phosphine–metal halide or metal carbonyl complexes, particularly $(Ph_3P)_2Ni(CO)_2$, which was discovered by Reppe and Sweckendiek,[1793] has been extensively investigated.[1799, 1801–7] Typical examples are the polymerization of 2-butyne-1,4-diol to hexamethylolbenzene,[1803] of phenylacetylene to 1,2,4-triphenylbenzene,[1801] and vinylacetylene to 1,2,4-trivinylbenzene[1799]:



α-ω Acetylenic hydrocarbons yield polymeric products.[1805] Kinetics of the polymerizations and the effects of the phosphine–metal carbonyl catalyst, acetylene structure and solvent are reported by Meriwether *et al.*,[1805–6] who showed that for complexes of the type $Ni(CO)_2,(PR_3)_2$ the catalytic activity varies as:

$$R = \text{—}CH_2CH_2CN > Ph > H > OEt > n\text{-alkyl} \gg \text{—}OPh \sim \text{zero}$$

### TERTIARY PHOSPHINE–ORGANOMETAL AND METAL HYDRIDE COMPLEXES

Organo and hydrido complexes of a number of metals having metal–carbon or metal–hydrogen bonds stabilized by tertiary phosphines have been prepared. Copper(I), silver(I) and gold(I) form ethynyl complexes of the type $PhC{\equiv}CM.PR_3$ ($M = Cu, Ag, Au$).[1817–8] A number of organogold compounds form tertiary phosphine complexes, $RAu.PR'_3$ ($R =$ alkyl, aryl); trimethylgold complexes, $Me_3Au.PR_3$ ($R = Me, Ph$), can be obtained by direct combination of $Me_3Au$ with the phosphine at −70°.[1852] Organonickel(II) and *cis-trans* planar platinum(II) compounds of the type $(R_3P)_2MR'X$ and $(R_3P)_2MR'_2$ ($M = Ni, Pt$; $R =$ alkyl, aryl, ethynyl; $X =$ halogen) can be obtained by treating the tertiary phosphine metal halide complexes $(R_3P)_2MX_2$ with Grignard or organolithium reagents.[1820–2, 1866, 1874] Platinum(IV) compounds $(Et_3P)_2Pt(Ph)_2X_2$ ($X = Cl, I$) are reported.[1821] Hydride complexes have been isolated in the cases of: planar platinum, $(R_3P)_2PtXH$ ($X = Cl, Br, CN, CNS$)[1819, 1824, 1831, 1866] and $[(Ph_3P)_3PtH]^+X^-$ ($X = Cl, NO_3, ClO_4, BF_4, BPh_4$)[1831]; iron, FeXH(diphosphine)$_2$ ($X = H$ or halogen)[1875–6]; nickel,[1865] ruthenium and osmium, *trans*-MXH(diphosphine)$_2$ ($X = Cl, Br, I, H, CNS, NO_2$)[1823, 1875]; iridium, $(Ph_3P)IrHCl_2$,[1825] $(Ph_3P)_3IrH_2Cl$[1825] and $(Ph_3P)_3IrH_3$.[1826]

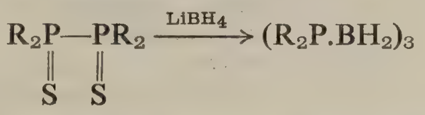
### PHOSPHINE–BORON HYDRIDE COMPLEXES

Boron hydrides react with primary and secondary phosphines to give 1 : 1 adducts which lose hydrogen, when heated, to form stable B–P polymers.[1388, 1780–1, 1867] The dimethylphosphine–borane complex, $Me_2PH,BH_3$, loses hydrogen at about 150° giving a mixture of a very stable and chemically inert trimeric dimethylphosphinoborane $(Me_2PBH_2)_3$, m.p. 86°, a somewhat less stable tetramer, m.p. 161°, and a trace of high polymer. The trimer is stable to heat below 350° and is hydrolyzed only slowly when heated at 300° with hydrochloric acid[1388, 1778, 1780]:

$$Me_2PH.BH_3 \xrightarrow[-H_2]{150°} (Me_2P.BH_2)_3 \xrightarrow{H_2O} 3Me_2PO_2H + 3H_3PO_4 + 12H_2$$

An *X*-ray diffraction study of the trimer indicates a *cyclo*hexane-like structure.[1755] The fully methylated phosphinoborane $(Me_2PBMe_2)_3$, m.p. 333°, is almost as stable to acid hydrolysis as $(Me_2P.BH_2)_3$; in contrast, $(H_2P.BMe_2)_3$ is rather unstable. Monomethylphosphine–borane complex is a volatile oil.[1388]

A number of other dialkylphosphinoboranes are described; they have been prepared by thermal decomposition of the dialkylphosphine–borane adduct,[1781] by reduction of $Me_2POCl$ or $Et_2PCl$ with $LiBH_4$[1780] and by reduction of tetra-alkyldiphosphine disulphides with alkali metal borohydrides[1870–1]:



$$\underset{\underset{S}{\|}}{R_2P}—\underset{\underset{S}{\|}}{PR_2} \xrightarrow{LiBH_4} (R_2P.BH_2)_3$$

Trimethylphosphine–borane, $Me_3P,BH_3$, is formed by direct reaction of trimethylphosphine with the borane, $B_2H_6$.[1388, 1872] A number of tertiary phosphine–borane adducts have been prepared by the exchange reaction[1868]:

$$Et_3N,BH_3 + R_3P \rightarrow R_3P,BH_3 + Et_3N\uparrow \qquad (R = \text{alkyl, aryl})$$

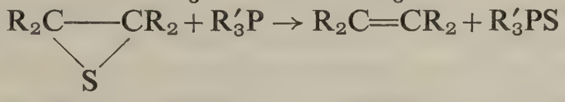
The reaction of phosphines with penta- and deca-borane are reported.[1867, 1869, 1873]

Enthalpies of reaction, in benzene solution, of diborane with mono-, di-, and triphenylphosphine have been determined calorimetrically and hence the enthalpies of the addition of these donors to $BH_3$ evaluated.[488]

### REDUCTION OF ORGANIC COMPOUNDS BY TERTIARY PHOSPHINES

The oxidation of trivalent phosphorus compounds has been reviewed by Cadogan.[355] Hydrogen peroxide, organic peroxides and disulphides, and many other oxygen and sulphur-containing compounds, are reduced by tertiary phosphines. In these reactions the phosphine is oxidized to the phosphine oxide or sulphide, e.g.

$$RO—OR + R'_3P \rightarrow ROR + R'_3PO$$



$$R_2C\underset{S}{\diagdown\!\diagup}CR_2 + R'_3P \rightarrow R_2C{=}CR_2 + R'_3PS$$

Some examples of the types of reductions which have been carried out, generally using triphenylphosphine, are shown in Table V.

## Derivatives of $P_2H_4$

Although the first organic derivative of diphosphine, $P_2H_4$, tetraphenyldiphosphine, was prepared in 1888 by Dörken[1883] by the interaction of diphenylphosphine and diphenylchlorophosphine, the chemical and physical properties of this compound remained largely unknown until the work of Kuchen and Buchwald[1884] was described in 1958. This work, together with that of Issleib and Seidel[68] who in 1959 described a number of tetra-alkyldiphosphines, forms the foundation for the recent rapid

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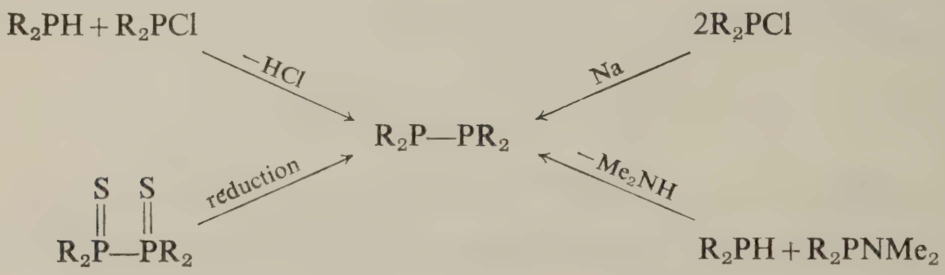
developments in this field. The chemistry of compounds with a P–P bond is reviewed by Cowley.[2171]

*Table V.—Reduction by Tertiary Phosphines*

| Class of organic compound | Product | Reference |
|---|---|---|
| Hydroperoxide | alcohol | 117, 118 |
| Dialkyl peroxide | ether | 117, 118 |
| Ozonide | ketone or aldehyde | 117, 119 |
| Peracid | carboxylic acid | 118, 122 |
| Perester | ester | 115, 118 |
| Diaryl peroxide | acid anhydride | 119–122 |
| Epoxides | olefine | 125, 185, 2003 |
| Episulphide | olefine | 126–128, 185 |
| Disulphide | thio ether | 110, 123, 178, 259, 261 |
| Tetrasulphide | disulphide | 260 |
| Arylsulphonyl chloride | mercaptan + disulphide | 128, 129 |
| Arylsulphinic acid | mercaptan | 129 |
| Arylsulphinyl chloride | mercaptan | 129 |
| Bis(*O*,*O*-dialkylthiophosphoryl) disulphide | trithiopyrophosphate | — |
| Amine oxide | amine | 124 |
| Nitroso compound | azoxy compound | 117, 868 |
| Aryl isocyanate | aryl isocyanide | 1693 |
| Oxazirane | imines | 262 |

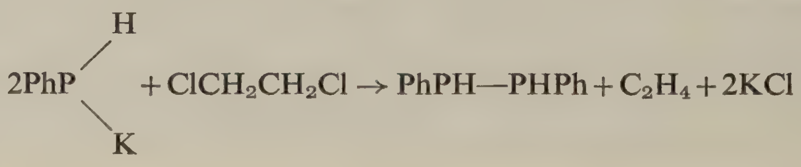
Tetrasubstituted diphosphines are generally prepared by the reaction of a secondary phosphine or its metal salt with a phosphinous chloride,[1884, 2172] by reduction of tetra-alkyldiphosphine disulphide with reagents such as zinc dust,[1903] sodium,[25] metals such as iron or calcium[30] or with tributylphosphine,[323, 1937] by reduction of phosphinous chlorides with metals,[26, 65, 68, 1884, 2173] and by reaction of secondary phosphine with *N*,*N*-dialkylphosphinous amides[296]:



Metal salts of certain secondary phosphines, particularly di*cyclo*hexylphosphine, react with alkyl halides such as ethylene dichloride,[85, 1879] ethyl iodoacetate[86] or triphenylmethyl chloride[212] to give tetrasubstituted diphosphines as the major product rather than the expected tertiary or ditertiary phosphine:

$$R_2PLi + ClCH_2CH_2Cl \rightarrow R_2PCl + LiCH_2CH_2Cl$$
$$LiCH_2CH_2Cl \rightarrow C_2H_4 + LiCl$$
$$R_2PLi + R_2PCl \rightarrow R_2P—PR_2 + LiCl$$

1,2-Diphenyldiphosphine results from the action of monopotassium phenylphosphine on ethylene dichloride or methylene dichloride,[76] the overall reaction being:



$$2PhP\begin{smallmatrix}H\\ \\K\end{smallmatrix} + ClCH_2CH_2Cl \rightarrow PhPH—PHPh + C_2H_4 + 2KCl$$

Diethylphosphinothionic chloride is reduced in good yield to $Et_4P_2$ by copper bronze.[30]

Reduction of asymmetric diphosphine disulphides $[RMePS]_2$ (R = Et, Ph) with two equivalents of tributylphosphine gives a 1 : 1 mixture of the two isomeric *cis-trans* diphosphines RMeP–PMeR.[1888]

Tetraphenyldiphosphine is formed by the thermal decomposition of diphenylphenylcarbamoylphosphine[168]; analogously phenylbis(phenylcarbamoyl)phosphine yields tetraphenyl*cyclo*tetraphosphine[168] and tris(phenylcarbamoyl)phosphine yields elemental phosphorus[156]:

$$2Ph_2PCONHPh \xrightarrow{\Delta} Ph_4P_2 + (PhNH)_2CO + CO$$
$$4PhP(CONHPh)_2 \xrightarrow{\Delta} (PhP)_4 + 4(PhNH)_2CO + 4CO$$
$$4P(CONHPh)_3 \xrightarrow{\Delta} P_4 + 6(PhNH)_2CO + 6CO$$

The same phosphorus-containing products are formed together with tributyldichlorophosphorane by the reaction of the halogen compounds $Ph_2PCl$, $PhPCl_2$, and $PCl_3$ with tributylphosphine[213]:

$$Bu_3P + 2Ph_2PCl \rightarrow Ph_4P_2 + Bu_3PCl_2$$
$$4Bu_3P + 4PhPCl_2 \rightarrow (PhP)_4 + 4Bu_3PCl_2$$
$$3Bu_3P + 2PCl_3 \rightarrow 2P + 3Bu_3PCl_2$$

The Raman spectra of $Et_4P_2$ and $Cu_4P_2$ show the phosphorus–phosphorus emission band at 424 and 419 cm.$^{-1}$ respectively.[1890]

### REACTIONS OF DIPHOSPHINES

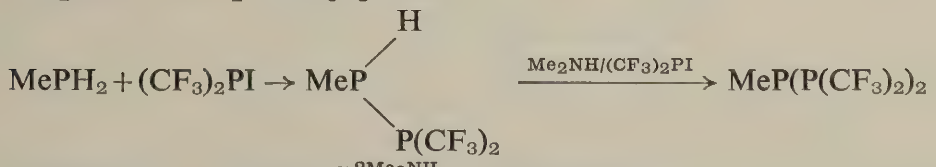
Like phosphines, tetrasubstituted diphosphines are extremely reactive compounds. The P–P bond is easily broken in reactions such as oxidation, reduction and halogenation. Reactions are shown in outline on Chart III.

## Derivatives of Linear Polyphosphines

The preparation and chemistry of organic polyphosphines to 1963 has been reviewed by Wiberg *et al.*[1881]

Various derivatives of $P_3H_5$ are reported, e.g., $Ph_5P_3$,[1884] $Et_5P_3$,[1881] $MeP(P(CF_3)_2)_2$,[1887] $P_3(CF_3)_5$,[1887] and $MeP(P(Ph)_2)_2$.[1900] Methods of preparation which are generally similar to those for diphosphine derivatives are indicated below:

$$2Ph_2PH + PhPCl_2 \rightarrow Ph_5P_3 + 2HCl$$



$$MePH_2 + (CF_3)_2PI \rightarrow MeP\begin{matrix} H \\ P(CF_3)_2 \end{matrix} \xrightarrow{Me_2NH/(CF_3)_2PI} MeP(P(CF_3)_2)_2$$

$$MeP(NMe_2)_2 + Ph_2PH \xrightarrow[\Delta]{-2Me_2NH} MeP(P(Ph)_2)_2$$

## *cyclo*Polyphosphines

Köhler and Michaelis in 1877 showed that phenylphosphine and phenyldichlorophosphine react with elimination of hydrogen chloride to give a compound of empirical formula PhP which was originally designated as phosphorobenzene, Ph–P=P–Ph, by analogy with azobenzene.[1891] The exact nature of the various polymeric forms of $(PhP)_n$ has been a matter of considerable controversy and it was not until the work of Daly and Maier was published that some light was shed on the subject.[1900, 2179–80, 2325, 2332] Crystalline compounds having the following melting

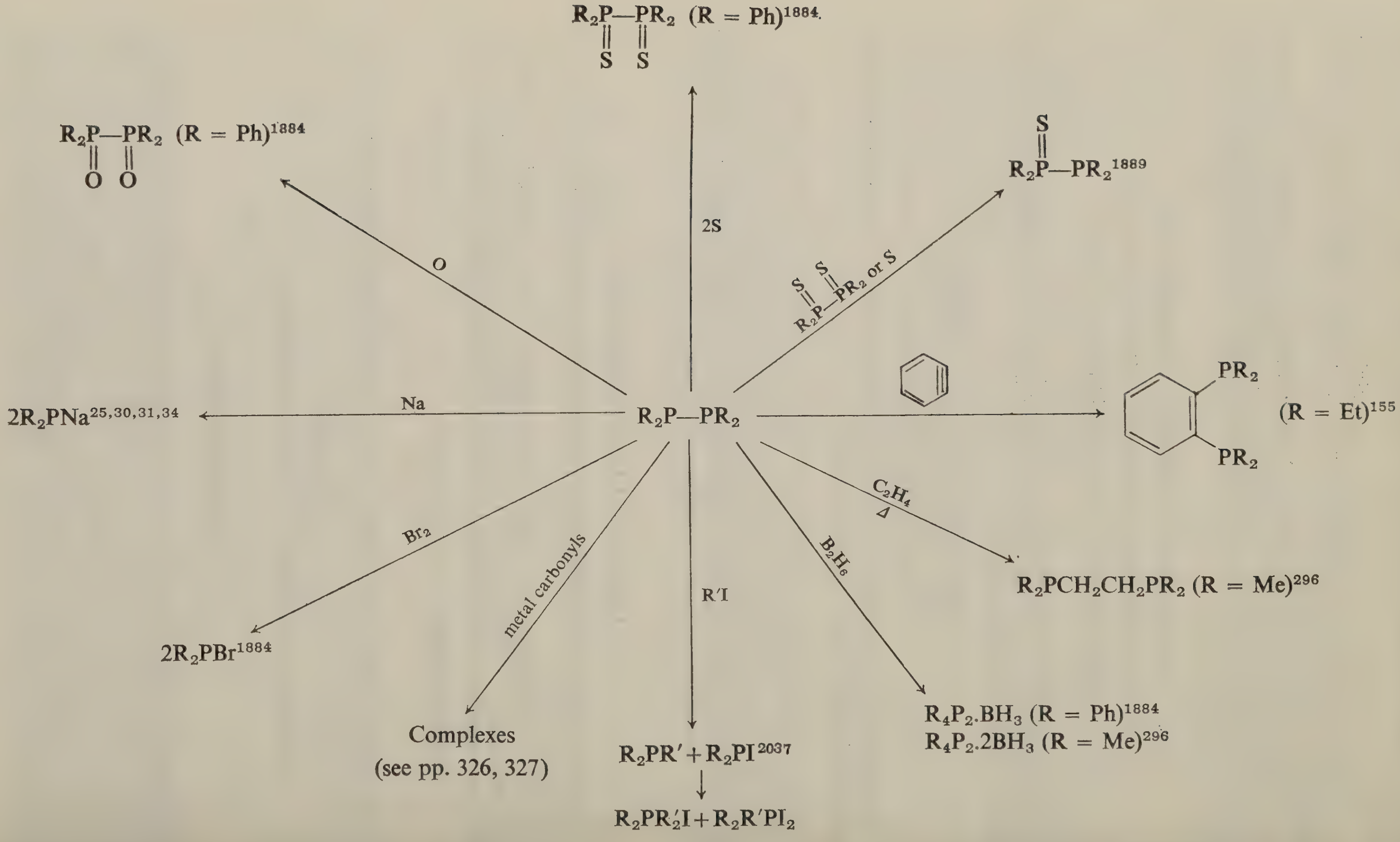
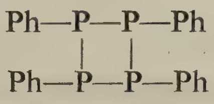


CHART III.—Some reactions of diphosphines points have been isolated: *A*, 149–150°[27,38,50,310,1881,1891,1894–5,1900,1905]; *B*, 154–156°[1900] (*A* recrystallized from methyl cyanide); *C*, 190°[310,1905]; *D*, 189–193°[1900] (*C* recrystallized from tetrahydrofuran, THF) together with amorphous, presumably polymeric, compounds having higher melting points which are insoluble in organic solvents.[1894,1900,1905]

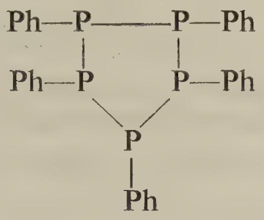
On the basis of molecular weight measurements of *A* and *C* in solution the following structures have been proposed: (i) *A*=*C*=**XXXVIII**[310]; (ii) *A*=**XXXVIII**, *C*=**XXXIX**[1905]; (iii) *A*=*C*=**XXXIX**[1894,1898]; and (iv) *A*=**XXXIX**[38,50,1881,1900,1907]

Ph—P=P—Ph

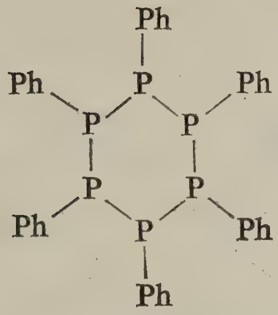
**XXXVIII**



**XXXIX**



**XL**



**XLI**

Henderson *et al.* concluded from cryoscopic, mass spectra and nuclear magnetic resonance data that *A* and *C*, both in the solid state and in solution, are stereoconformers of tetraphenyl*cyclo*tetraphosphine **XXXIX**[1894,1898] and found no evidence for the existence of **XXXVIII**. Daly and Maier determined the molecular weights, from cell dimensions and density of the crystalline compounds *B* and *D*, and determined their structure by *X*-ray crystal analysis. Compound *B* was shown to be pentaphenyl*cyclo*pentaphosphine, **XXXVIII**. Compound *D* crystallizes in at least four forms, all of which are crystalline modifications of hexaphenyl*cyclo*hexaphosphine, **XLI**. The *X*-ray powder patterns of the high-melting compounds, m.p. 252°–256° and 260°–285°, show these to be highly crystalline. The pentamer reacts with nickel carbonyl to form a complex and is cleaved by sulphur to form $(PhPS)_3$; the hexamer reacts with neither nickel carbonyl nor sulphur.[2325]

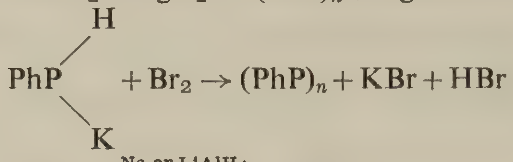
It is reported that whereas phosphorobenzene, $(PhP)_4$, reacts with $Ni(CO)_4$ or $[Fe(CO)_4]_2$ giving carbonyl derivatives $(PhP)_4,Ni(CO)_3$ and $(PhP)_4,[Fe(CO)_4]_2$ respectively, carbonyls of molybdenum and tungsten form complexes of the type $(PhP)_5,M(CO)_5$.[1901] Expansion of a 4-membered to a 5-membered phosphorus ring was postulated.[1901] Daly and Maier point out that preparation of compound B in two ways and crystallization from three different solvents, benzene/ethanol, acetonitrile or tetrahydrofuran, always gave crystals of the pentamer and suggest that synthesis of $(PhP)_4,NiCO_3$ could be equally well explained by postulating a ring contraction of $(PhP)_5$.[2332] At 160° phosphobenzene decomposes giving phenylphosphindene, PhP, a reactive intermediate which can be trapped by reaction with disulphides to form a phenyl phosphonodithioite[194]:

$$(PhP)_n \rightarrow PhP \xrightarrow{Et_2S_2} PhP(SEt)_2$$

Other methods of preparing phosphorobenzene are the reaction of phenylphosphine with tetramethylphenylphosphonous diamide[1900,2325] or with an organo-mercury compound,[1895] by the action of bromine on monopotassiumphenylphosphine,[76] and by reduction of phenylphosphonous dichloride[50]:

$$2PhP(NMe_2)_2+2PhPH_2 \xrightarrow{170°/1\ hr.} (PhP)_5+4Me_2NH$$

$$PhPH_2+HgR_2 \rightarrow (PhP)_n+Hg+2RH$$

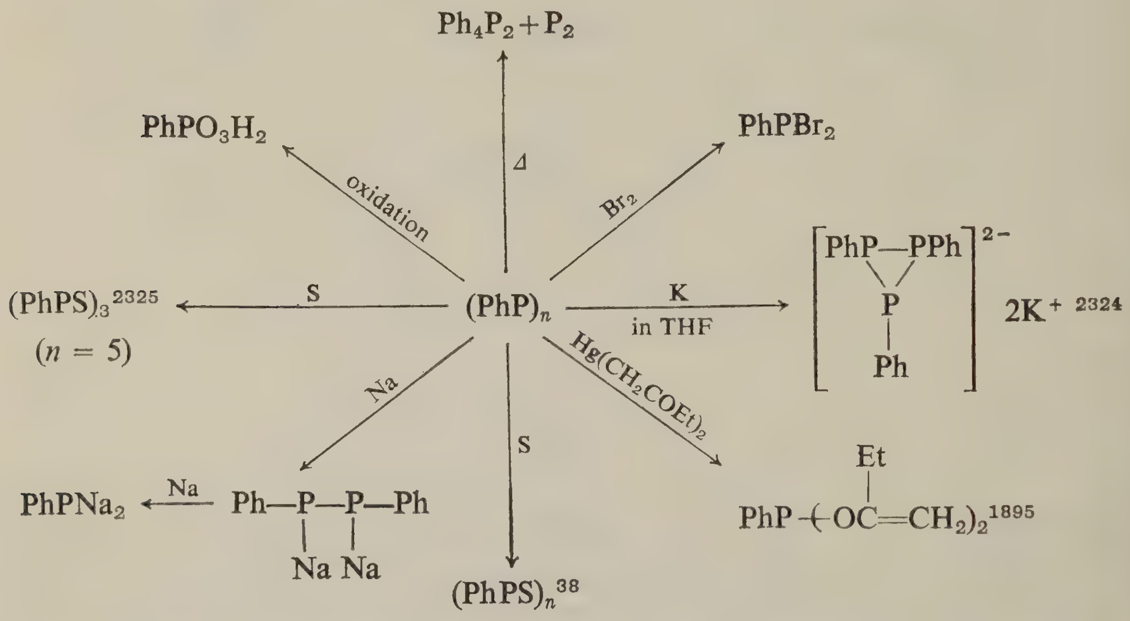


$$PhP\begin{smallmatrix}H\\K\end{smallmatrix} + Br_2 \rightarrow (PhP)_n + KBr + HBr$$

$$PhPCl_2 \xrightarrow{Na\ or\ LiAlH_4} (PhP)_n$$

The fluorinated pentameric *cyclo*polyphosphine $(C_6F_5P)_5$ is made by reaction of pentafluorophenylphosphonous dibromide or di-iodide with elemental mercury.[2326]

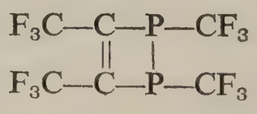
Some reactions of $(PhP)_n$ are indicated below:



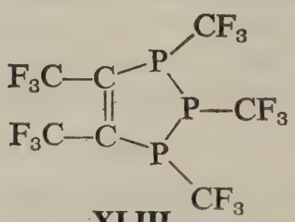
The first alkyl*cyclo*polyphosphines, tetrameric and pentameric trifluoromethyl compounds $(CF_3P)_4$ and $(CF_3P)_5$, were prepared in 1958 by Mahler and Burg[1892] by the reduction of trifluoromethylphosphonous di-iodide with elemental mercury at room temperature:

$$CF_3PI_2+Hg \rightarrow (CF_3P)_4 \quad \text{m.p. } 66{\cdot}4°,\ \text{b.p. } 145°$$
$$(CF_3P)_5 \quad \text{m.p. } -33°,\ \text{b.p. } 190°$$

*X*-Ray crystal analysis of the tetramer shows a puckered 4-membered phosphorus ring.[1897] The two compounds react easily and reversibly with trimethylphosphine or trimethylamine to form the complexes $Me_3P–PCF_3$ and $Me_3N–PCF_3$ respectively. These dissociate at room temperature to a mixture of $(CF_3P)_4$ and $(CF_3P)_5$.[1907] Catalytic amounts of trimethylphosphine suffice to convert $(CF_3P)_5$ to $(CF_3P)_4$ at room temperature; in the absence of this catalyst interconversion takes place at 260°.[1907] Reaction of the tetramer and pentamer with bistrifluoromethylacetylene yields 1,2,3,4-tetrakis(trifluoromethyl)-3,4-diphospha*cyclo*butene, **XLII**, and 1,2,3,4,5-pentakis(trifluoromethyl)- 3,4,5-triphospha*cyclo*pentane **XLIII**[1899]:



**XLII**

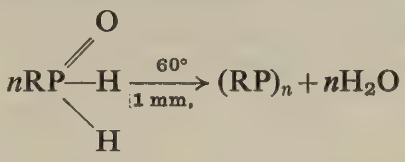


**XLIII**

Pentamethyl*cyclo*pentaphosphine has been synthesized by the thermal decomposition of methyl phosphonodifluoridite,[302]

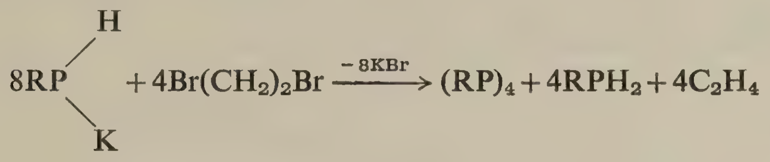
$$(\mathrm{MePF_2} \xrightarrow{\Delta} (\mathrm{MeP})_5)$$

A number of alkyl *cyclo*polyphosphines $(RP)_4$ and $(RP)_5$ have been synthesized by the condensation of monoalkylphosphine with alkylphosphonous dichloride,[1886] by reduction of the phosphonous dichloride with magnesium or lithium and by dehydration of primary phosphine oxides[1894, 1896]:

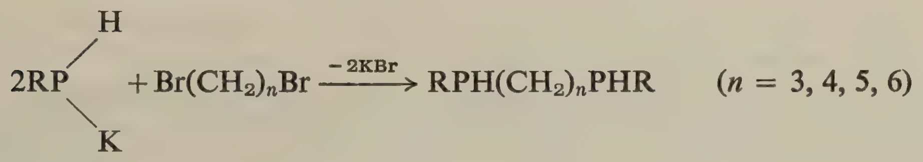


$$n\mathrm{RP}(=\mathrm{O})(\mathrm{H})\mathrm{-H} \xrightarrow[1\ \mathrm{mm.}]{60^\circ} (\mathrm{RP})_n + n\mathrm{H_2O}$$

Tetrabutyl*cyclo*tetraphosphine is obtained in 42% yield by the reaction of white phosphorus with butyl magnesium bromide and butyl bromide.[18] Tetra*cyclo*hexyltetraphosphine, $(RP)_4$, is formed by the action of potassium *cyclo*hexyl phosphide on methylene dichloride or ethylene dibromide[79]; the 1,3-, 1,4-, 1,5- and 1,6-dihalides yield the expected disecondary phosphines:

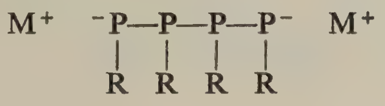


$$8\mathrm{RP}(\mathrm{H})(\mathrm{K}) + 4\mathrm{Br(CH_2)_2Br} \xrightarrow{-8\mathrm{KBr}} (\mathrm{RP})_4 + 4\mathrm{RPH_2} + 4\mathrm{C_2H_4}$$



$$2\mathrm{RP}(\mathrm{H})(\mathrm{K}) + \mathrm{Br(CH_2)}_n\mathrm{Br} \xrightarrow{-2\mathrm{KBr}} \mathrm{RPH(CH_2)}_n\mathrm{PHR} \qquad (n = 3, 4, 5, 6)$$

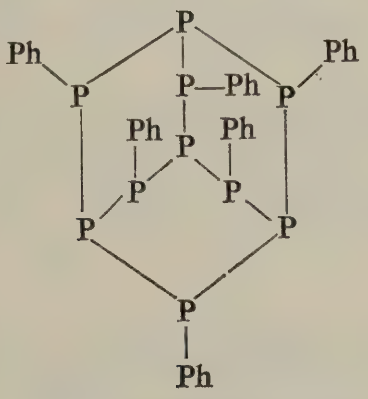
Metal phosphides of the type:



$$\mathrm{M^+}\quad {}^-\underset{\mathrm{R}}{\mathrm{P}}-\underset{\mathrm{R}}{\mathrm{P}}-\underset{\mathrm{R}}{\mathrm{P}}-\underset{\mathrm{R}}{\mathrm{P}}^-\quad \mathrm{M^+}$$

(R = ethyl, methyl; M = Li, Na, K; R = *cyclo*hexyl; M = K) are formed by the action of the metals on the *cyclo*tetraphosphines $(RP)_4$ in tetrahydrofuran solution. They react with alkyl halides giving linear tetraphosphines.[2327] Complexes of *cyclo*polyphosphines with boron halides[2328] and with copper halides[2329] are reported.

A compound $Ph_6P_{10}$, believed to have an adamantane-like structure, **XLIV**, has been obtained by the interaction of dilithiumphenylphosphine with phosphorus trichloride[1881].

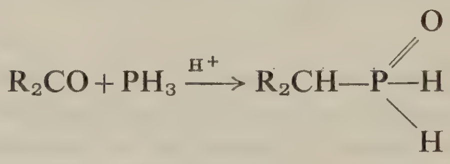


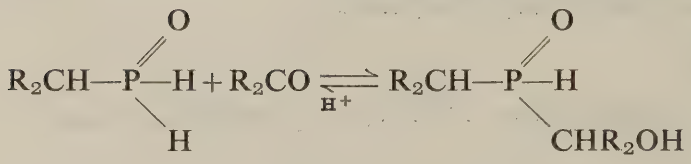
**XLIV**

## PHOSPHINE OXIDES AND RELATED COMPOUNDS

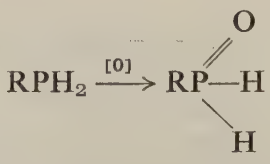
### Primary Phosphine Oxides, $RPOH_2$

Buckler and Epstein in 1960[102] showed that phosphine reacts with ketones in concentrated hydrochloric acid solution to form a mixture of the corresponding primary phosphine oxide and α-hydroxyalkyl secondary phosphine oxide. The primary oxide is formed initially by a reaction which involves migration of an oxygen atom from carbon to phosphorus; the secondary oxide is formed subsequently by a normal carbonyl addition to the primary oxide:





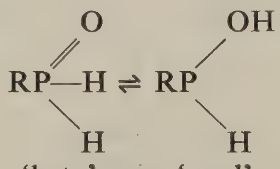
The relative amounts of the two products formed are determined by steric factors which influence the extent to which the carbonyl addition occurs.[102, 1909–10] Primary phosphine oxides may also be prepared by the controlled oxidation of primary phosphines with hydrogen peroxide in ethyl alcohol under an atmosphere of nitrogen,[102–3, 1909] by *tert*-butyl hydroperoxide[103] or by nitrogen dioxide[103]:



Although stable in hydrochloric acid solution or at low temperature, primary phosphine oxides readily disproportionate in alcohol solution or in concentrated form at room temperature to form a mixture of primary phosphine and phosphonous acid.[1909] They are also readily dehydrated giving *cyclo*polyphosphines[1894, 1896]:

$$2RPO.H_2 \rightarrow RPH_2 + RPO_2H_2$$
$$nRPO.H_2 \xrightarrow[1\text{ mm.}]{60^\circ} (RP)_n + nH_2O$$

For this reason primary phosphine oxides have generally been characterized by infra-red and nuclear magnetic resonance spectroscopy and by conversion to derivatives (see Chart IV). Spectroscopic data show the compounds to exist mainly in their ‘keto’ rather than their ‘enol’ forms[1909]:



'keto' 'enol'

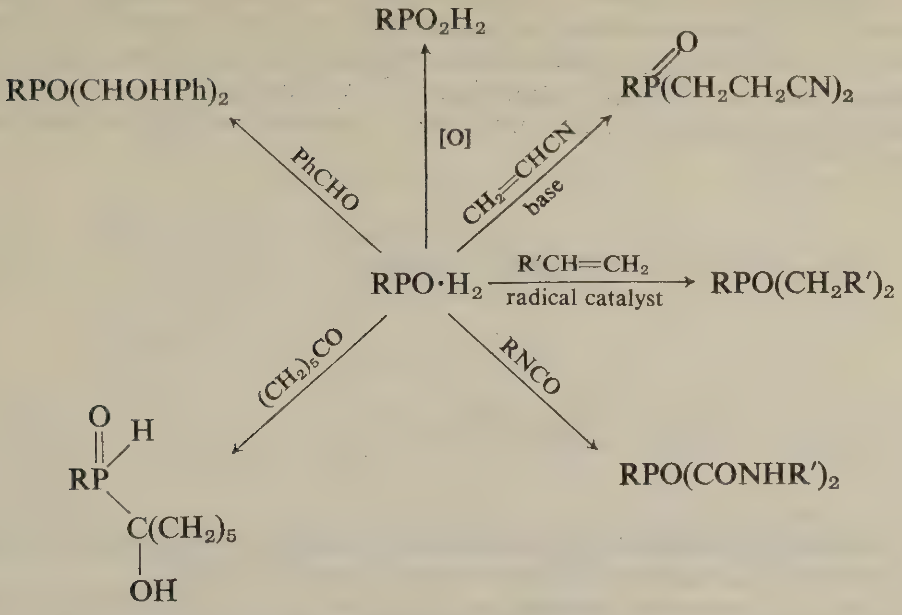
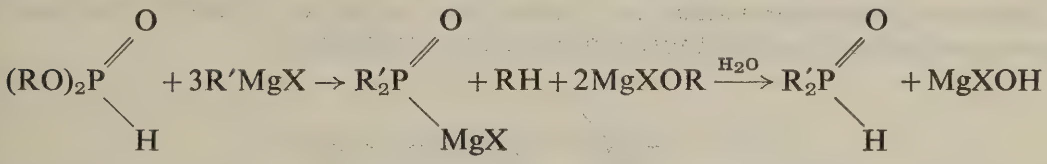


CHART IV.—Some reactions of primary phosphine oxides

## Secondary Phosphine Oxides, $R_2\overset{O}{\underset{H}{P}}$

Dialkyl phosphine oxides were first obtained by Williams and Hamilton in 1952 by the reaction of dialkyl hydrogen phosphonates with Grignard reagents.[1911] A number of other routes to these compounds are now well established but the Grignard synthesis, owing to the availability of starting compounds and high yields, remains the most convenient laboratory method for dialkylphosphine oxides in which the alkyl groups are unsubstituted butyl or higher alkyls (lower dialkyl compounds have not been isolated):

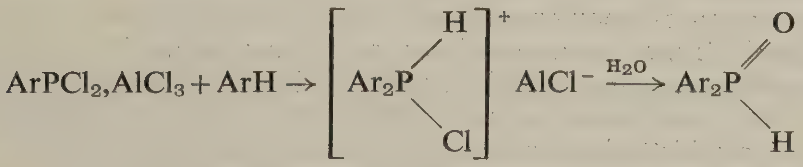


$$(RO)_2\overset{O}{\underset{H}{P}} + 3R'MgX \rightarrow R'_2\overset{O}{\underset{MgX}{P}} + RH + 2MgXOR \xrightarrow{H_2O} R'_2\overset{O}{\underset{H}{P}} + MgXOH$$

(R = ethyl, butyl; R' = butyl,[282] higher alkyl,[444, 1911] phenyl[1913, 1915]).

Organolithium compounds have been used in place of the Grignard reagents.[1914] Diarylphosphine oxides are best prepared by the Friedel–Crafts reaction of phosphorus trichloride with an excess of an aromatic hydrocarbon[1918]:

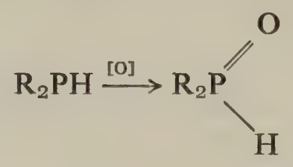
$$PCl_3 + ArH + AlCl_3 \rightarrow ArPCl_2,AlCl_3 + HCl \uparrow$$



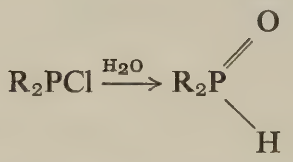
$$ArPCl_2,AlCl_3 + ArH \rightarrow \left[Ar_2\overset{H}{\underset{Cl}{P}}\right]^+ AlCl^- \xrightarrow{H_2O} Ar_2\overset{O}{\underset{H}{P}}$$

Small yields of diarylphosphine oxides have been reported as by-products in the conventional Friedel–Crafts synthesis of arylphosphonous dichlorides when the aromatic function was mesityl, durenyl, and pentamethylphenyl.[1914]

Other methods of preparation are the carefully controlled oxidation of secondary phosphines,[104-6] the hydrolysis of dialkyl[284,1914] or diaryl[424,532] phosphinyl chlorides, the reduction of phosphinyl chlorides with reagents such as lithium aluminium hydride, $LiAlH_4$, magnesium[1916] or sodium[1916] and the reaction of ketones with phosphine in the presence of concentrated hydrochloric acid (see p. 916).[102,1909-10]



$$R_2PH \xrightarrow{[O]} R_2P(=O)H$$



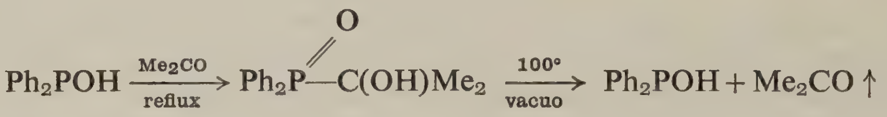
$$R_2PCl \xrightarrow{H_2O} R_2P(=O)H$$

Sodium diphenylphosphine oxide results from the action of sodium hydroxide,[36] sodium hydride[1926] or sodium[1928] on triphenylphosphine oxide.

The majority of secondary phosphine oxides are colourless crystalline solids. The diaryl compounds are unstable on storage or during attempted distillation, disproportionating to a mixture of secondary phosphine and phosphinic acid:

$$2R_2POH \rightarrow R_2PH + R_2PO_2H$$

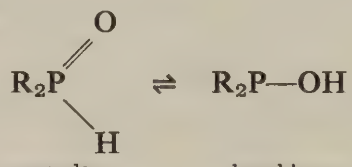
They are conveniently isolated as their crystalline acetone[1918] or chloral[532] adducts. Diphenylphosphine oxide may be stored as its acetone complex which dissociates on heating to regenerate the phosphine oxide:



$$Ph_2POH \xrightarrow[\text{reflux}]{Me_2CO} Ph_2P(=O)\text{—}C(OH)Me_2 \xrightarrow[\text{vacuo}]{100^\circ} Ph_2POH + Me_2CO\uparrow$$

Dialkylphosphine oxides disproportionate less readily than the aryl compounds. Di-*n*-butylphosphine oxide disproportionates at 220° to dibutylphosphine and dibutyl phosphinic acid[282]; dioctylphosphine oxide is reported to be stable for several hours at 200°–250°, but disproportionates in the presence of sodium hydroxide.[284]

Secondary phosphine oxides and phosphinous acids are isomeric; they may be represented as keto and enol forms of the same compound:



$$R_2P(=O)H \rightleftharpoons R_2P\text{—}OH$$

secondary phosphine oxide    phosphinous acide

The structure of secondary alkyl and arylphosphine oxides is indicated from potentiometric titrations which show them to be neutral compounds,[444,1911] and by their infra-red spectra, which show the presence of P=O and P–H bonds but no P–OH bond.[1924] Equilibrium with the phosphinous acid structure is indicated by the preparation of silver diphenylphosphinate from diphenylphosphine oxide and silver nitrate solution[1913]; the formation of this salt is slow, suggesting a slow rearrangement of phosphine oxide to phosphinous acid. Although many esters of phosphinous acids, $R_2P\text{–}OR'$, have been prepared,[329,411,413,525-7,544,576-7,1919] the only true acids reported are bis(trifluoromethyl)phosphinous acid, $(CF_3)_2P\text{–}OH$,[1923] and its sulphur analogue bis-(trifluoromethyl)thiophosphinous acid, $(CF_3)_2PSH$.[583] The oxygen compound forms salts such as $(CF_3)_2PO^-\ Me_3\overset{+}{N}H$; its infra-red spectrum shows the presence of a P–OH bond but no P=O or P–H bonds.

Secondary phosphine oxides undergo numerous reactions characteristic of compounds having a P–H bond, such as base-catalyzed addition to carbonyl compounds, negatively substituted olefins and isocyanates and free-radical catalyzed addition to olefins to form unsymmetrical tertiary phosphine oxides.

$$R_2PO.H \xrightarrow{R'_2CO + \text{Base}} R_2PO.CH(OH)R'_2{}^{105,1915}$$

$$R_2PO.H \xrightarrow{CH_2{=\!=}CHX + \text{Base}} R_2PO.CH_2CH_2X \quad (X = CN, CO_2R, COCH_3, CONH_2)^{104-5,1917}$$

$$R_2PO.H \xrightarrow{ArNCO + \text{Base}} R_2PO.CONHAr^{105}$$

$$R_2PO.H \xrightarrow{R'CH{=\!=}CH_2 + R^{\cdot}} R_2PO.CH_2CH_2R'$$

Active aldehydes such as chloral and formaldehyde react readily in the absence of base catalysts[104-5] particularly with the more 'acidic' secondary phosphine oxides such as diarylphosphine oxides[532,1918] and bis(-2-cyanoethyl)phosphine oxide.[105]

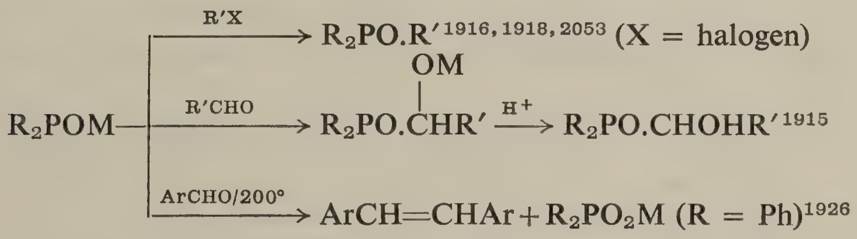
The compounds may be halogenated giving phosphinyl halides, undergo the Mannich reaction to form $\beta$-dialkylaminomethyl tertiary phosphine oxides and react with carbon tetrachloride and alcohols in the presence of tertiary organic amines to form alkyl phosphinates (cf. the Todd reaction p. 991).

$$R_2PO.H \xrightarrow{N\text{-chlorosuccinimide}/SOCl_2} R_2PO.Cl^{284,1913}$$

$$R_2PO.H \xrightarrow{CH_2O + R_2NH} R_2PO.CH_2NR_2{}^{105}$$

$$R_2PO.H \xrightarrow{CCl_4,\ R'OH,\ R_3N} R_2PO.OR'^{105}$$

Metal salts of secondary phosphine oxides are alkylated by alkyl halides to unsymmetrical tertiary phosphine oxides; they react with carbonyl compounds to form salts of $\alpha$-hydroxyphosphine oxides. Aromatic aldehydes and salts of diphenylphosphine oxide react at 200° in a Wittig-type reaction to form stilbene derivatives:



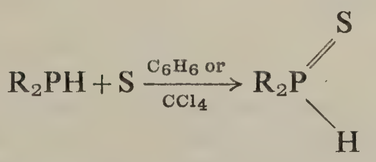
$$R_2POM \xrightarrow{R'X} R_2PO.R'^{1916,1918,2053} \quad (X = \text{halogen})$$

$$R_2POM \xrightarrow{R'CHO} R_2PO.\overset{\overset{OM}{|}}{C}HR' \xrightarrow{H^+} R_2PO.CHOHR'^{1915}$$

$$R_2POM \xrightarrow{ArCHO/200^\circ} ArCH{=}CHAr + R_2PO_2M \quad (R = Ph)^{1926}$$

## Secondary Phosphine Sulphides, $R_2PS.H$

These compounds were first prepared by Peters in 1960[131]; they are obtained by the careful addition of sulphur to secondary phosphines in inert solvent solution[66,131,1747]:



$$R_2PH + S \xrightarrow[CCl_4]{C_6H_6 \text{ or}} R_2P(S)H$$

Two new routes to secondary phosphine sulphides are the reaction of *N*,*N*-dimethyl phosphinamides with hydrogen sulphide and the action of organo-lithium compounds on diethyl hydrogen phosphonothionate[2330]

$$RR'PNMe_2 \xrightarrow[\text{in benzene at } 80^\circ]{H_2S} RR'P(S)H$$

$$(EtO)_2P(S)H \xrightarrow{RLi} Et_2P(S)H$$

**Refs. p. 1082**

The thiono structure has been confirmed by nuclear magnetic resonance and infrared spectroscopy. They undergo base catalyzed addition to carbonyl compounds forming α-hydroxyalkyl tertiary phosphine sulphides, are chlorinated to form phosphinochloridothionates, react with sulphur to form phosphinodithioic acids, and add to olefins in the presence of radical catalysts giving tertiary phosphine sulphides.

Secondary phosphine selenides, $R_2P(Se)H$ ($R = Ph$, $Me_2CHCH_2^-$), have been made by adding red selenium to the secondary phosphines in benzene solution. They have the same structure as the corresponding oxides and sulphides but are less reactive and do not add to acetone in the presence of basic catalysts.[2177]

### Tertiary Phosphine Oxides, $R_3PO$

The chemistry of secondary and tertiary phosphine oxides to 1960 has been reviewed by Berlin and Butler.[1908]

As a class, tertiary phosphine oxides are the most stable organophosphorus compounds. The carbon–phosphorus bonds are comparable in strength with C–C bonds[456] and will remain intact under quite vigorous reaction conditions. For example, $Ph_3PO$ may be nitrated with nitric-sulphuric acid mixtures to form $(m\text{-}NO_2\text{-}C_6H_4)_3PO$[1]; methyl substituents on the aryl groups of compounds of the type $RPO.(C_6H_4Me)_2$ ($R = Me$, Et, Ph) may be oxidized to carboxyl groups using alkaline permanganate in aqueous pyridine[1882,1956] without cleaving the C–P bond. Tertiary phosphine oxides generally possess a high degree of thermal stability, the temperatures required for decomposition being approximately 300°C. above those required for decomposition of the corresponding amine oxides.[1700] Oxides having alkyl groups with an available β-hydrogen atom cleave to olefin and secondary phosphine oxides; oxides having no β-hydrogen atom are more stable. The secondary phosphine oxide formed by thermal decomposition of the lower members undergoes disproportionation, e.g., ethyldimethylphosphine oxide decomposes:

$$\begin{array}{l} Me_2EtPO \xrightarrow{330^\circ\text{–}670^\circ} Me_2POH + C_2H_4 \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\quad Me_2PH + Me_2PO_2H \end{array}$$

Relative stabilities of several phosphine oxides are shown in Table VI.[1700]

*Table VI.—Relative Stabilities of Several Phosphine Oxides*

| R in RR′R″PO | Temperature for 50% decomposition |
|---|---|
| $Me_3$ | stable to 700° |
| $Ph_3$ | slight discoloration at 690° |
| Et, Me, Ph | 665° |
| $Me_2$, Et | 525° |
| $Et_3$ | 510° |
| Et, Me, pentyl | 490° |
| $Bu_3$ | 490° |

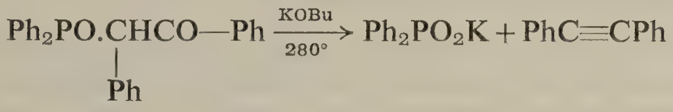
Notable exceptions to the general stability are (a) α-hydroxyalkyl substituted phosphine oxides, which undergo C–P fission with aqueous bases[36,273,1915] and dissociate on heating,[424,1915] (b) tris-(2-pyrryl)phosphine oxide which, gives pyrrole on cleavage with aqueous base,[1986] and (c) tris-(trifluoromethyl)phosphine oxide which, in turn, is decomposed by water to bis-(trifluoromethyl)phosphinic acid or by aqueous base to trifluoromethylphosphonic acid.[1962] Benzyl[1968] and aryl[36,1970] substituted phosphine oxides undergo C–P bond fission on fusion with sodium hydroxide to yield sodium phosphinate and hydrocarbon, e.g.,

$$Ph_3PO \xrightarrow[\Delta]{NaOH} Ph_2PO_2Na + PhH$$

In this reaction the ease of substituent fission in unsymmetrical tertiary phosphine oxides decreases in the series: benzyl > phenyl > alkyl, and naphthyl > phenyl > *p*-tolyl.[1970] Alkali metal salts of secondary phosphine oxides are formed by fusion of aryl-substituted phosphine oxides with alkali metals[1928] or with sodium hydride,[1926] e.g.,

$$Ph_3PO \xrightarrow{NaH} Ph_2PONa + PhH$$

*β*-Keto substituted alkylphosphine oxides are decomposed by bases at high temperatures giving phosphinate and acetylene[1920]:



$$\underset{\displaystyle Ph}{Ph_2PO.\underset{|}{C}HCO—Ph} \xrightarrow[280°]{KOBu} Ph_2PO_2K + PhC{\equiv}CPh$$

Attempts to reduce tertiary phosphine oxides to tertiary phosphines, except by the use of metal hydrides (see p. 895), have been unsuccessful. Recently reported reduction techniques involve the use of silicon hydrides such as polymethyl siloxane[40] or silicochloroform[1982] and boranes or trialkylamine boranes[2179] as reducing agents:

$$R_3PO + 2SiCl_3H \rightarrow R_3P + SiCl_4 + H_2 + (Cl_2SiO)_n$$
$$R_3PO + SiCl_3H + R_3N \rightarrow R_3P + R_3N,HCl + (Cl_2SiO)_n$$
$$Ph_3PO + (R_2BH)_2 \rightarrow Ph_3P + (R_2B)_2O + H_2$$

The atomic refractions of phosphorus in tertiary phosphine oxides are given by Razumov and Zabusova.[1977]

Electron diffraction of trimethylphosphine oxide in the gas phase shows bond lengths P–O 1·48 A., P–C 1·81 A., and bond angles C–P–C 106°, C–P–O 112·3°.[2333]

### TERTIARY PHOSPHINE OXIDE COMPLEXES

Phosphine oxides readily form hydrates, generally monohydrates, $R_3PO,H_2O$ and less frequently the hemihydrate $(R_3PO)_2,H_2O$. Triphenylphosphine oxide forms a hydrate, m.p. 132°, and a hemihydrate, m.p. 154–157°. A hydrogen peroxide adduct $(Ph_3PO)_2,H_2O_2$ is reported to be formed when triphenylphosphine is oxidized by aqueous hydrogen peroxide.[1992] Using $^{18}O$-labelled $Ph_3PO$ it has been demonstrated that no oxygen exchange occurs with water even at the boiling point.[1973] Tertiary phosphine oxides are weakly basic[1972]; they form adducts with many simple and complex inorganic acids[265, 1972] and with strong organic acids such as trichloroacetic acid,[1991] many of which are stable crystalline compounds having characteristic melting points. Spectrophotometric studies of $R_3PX$ ($X = O, S, Se$) complexes with halogens, such as iodine, iodine chloride and bromide, show that in cases where the 1:1 complex is the principal one, and when the substituents on phosphorus are identical, there is a considerable increase in the formation constant which follows the sequence $Se > S > 0$.[1985, 1993] Alkali metals are reported to form highly coloured adducts with tertiary phosphine oxides.[1974]

Co-ordination compounds having tertiary phosphine oxide ligands have been prepared from many metal salts particularly those of the transition metals. Complexes are reported of the types: $(R_3PO)_2,Y$ (where $Y = SnCl_4$, $SnBr_4$, $FeBr_2$, $TiCl_4$,[1965] $SbCl_5$,[1684] $FeCl_2$, $InCl_3$, $SiCl_4$, $SnI_4$, $AsCl_3$, $SbCl_3$, $BiCl_3$, $BiBr_3$, $BiI_3$[1930]); $Ph_3PO,X$ (where $X = MgCl_2$, $BF_3$, $BBr_3$, $AlCl_3$, $GaCl_3$, $InCl_3$, $TiCl_4$, $PCl_5$[1930]); $(R_3PO)_2,MX_2$ (where M = Zn,[1925,1953,1972] Cd,[1953,1972] Cu,[1925,1944] Fe,[1953] Co,[67,88,1936,1953,1966,1972] Ni,[67, 88, 1932, 1966] Hg,[1684, 1972] Mn,[1938, 1953] Cr,[1967] and X = univalent anion); $(alkyl_3PO)_3,Cr(CNS)_3$[1967]; $(Ph_3PO)_3,CrCl_3$[1930]; $3R_3PO,Fe_2Cl_6$[1925]; and $[(R_3PO)_4M]^{n+}X_n^-$ ($M = Mn^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$ and $X = ClO_4$).[1958]

This property has been utilized in a number of analytical methods which involve the separation of metals by solvent extraction.[1964] The use of tertiary phosphine oxides as extractants for uranium and thorium has been extensively investigated.[1521, 1647, 1927, 1929]

Although numerous tertiary phosphine oxide–metal halide complexes are known, only a few complexes of tertiary phosphine sulphides and selenides are described; these are: $(Ph_3PS)_2,PdCl_2$,[1307] $(R_3PS)_2,SnX_4$ (R = alkyl, X = Cl, Br),[1301] $(Ph_3PSe)_2,PdCl_2$,[1307] $(Ph_3PSe)_2,SnCl_4$,[1307] and $Ph_3PS,Y$ (where Y = $HgCl_2$, $AlCl_3$, $AlBr_3$, $SnCl_4$, $TiCl_4$, $TiBr_4$, $SbCl_5$, $NbCl_5$, $TaCl_5$, $FeCl_3$).[2331]

## PREPARATION OF TERTIARY PHOSPHINE OXIDES

Tertiary phosphine oxides are generally prepared either by direct oxidation of the corresponding phosphine or by reaction of a pentavalent phosphoryl halide or ester with an organometallic compound such as a Grignard reagent. The halogen atoms of phosphoryl halides and the alkoxyl (or aryloxy) groups of phosphate esters may be replaced with moderate success in a stepwise manner by Grignard reagents and to obtain tertiary phosphine oxide it is general to use a slight excess of the reagent. The following phosphorus-containing starting materials may be used: phosphorus oxyhalides,[95, 1946–50, 1972] phosphonyl halides,[1951, 1956] phosphinyl halides,[1951–2, 1978] dialkyl phosphorochloridates,[465] tertiary phosphates,[1955] phosphonates,[1954, 1956] and phosphinates.[1957] Organolithium compounds have been used to prepare tertiary phosphine oxides from phosphorus oxyhalides,[219] trialkyl phosphates,[1959] and diethyl phosphorochloridate[1960]:

$$POX_3 \xrightarrow[3RLi]{3RMgX} R_3PO + 3MgX_2 \text{ (or LiX)}$$

Pyrophosphoryl chloride reacts with phenyl magnesium halides to give a mixture of triphenylphosphine oxide and diphenylphosphinic acid.[1975] Phosphorus pentachloride (see p. 891) gives a mixture of products.

### *Miscellaneous Methods*

Tertiary phosphine oxides are formed as the isolable products after hydrolysis from the reaction of elemental phosphorus[20, 22] or phosphorus and $P_2I_4$[23, 238] or $P_2I_4$[2294] with alkyl iodides (p. 885), and by the alkaline decomposition of many quaternary phosphonium salts (p. 937). Good yields of tris-($\beta$-substituted)phosphine oxides result from the action of aqueous alkali on white phosphorus in the presence of negatively substituted olefines such as acrylonitrile or acrylamide and tetrafluoroethylene[1671, 1922]:

$$P_4 + KOH + CH_2{=}CHX \xrightarrow{H_2O} OP(CH_2CH_2X)_3$$
$$(X = CN, CONH_2, CO_2R, SO_2Me)$$

Tris(dialkylaminomethyl)phosphine oxides are formed in high yield by the reaction of white phosphorus with *N*-hydroxymethyldialkylamines in water–alcohol mixture at 80°C.[2002]

Dihalogenophosphoranes react readily with water, alcohols[22, 1987] or anhydrous oxalic acid[1962] to form the phosphine oxide:

$$R_3PX_2 \xrightarrow{R'OH} R_3PO + R'X + HX \qquad (R' = H, \text{alkyl})$$

Dihalogenophosphoranes have been proposed as reagents for the preparation of optically pure, inverted, alkyl halides from optically active alcohols, and neopentyl halides which are free of isomeric halide from neopentyl alcohol[1988–9]:

$$Ph_3PX_2 + ROH \rightarrow [Ph_3\overset{+}{P}OR\,X^- + HX] \rightarrow Ph_3PO + RX + HX$$

A related reaction is that of a tertiary phosphine with monobromocyanoacetamide and a reactive alcohol such as benzyl or allyl alcohol, the overall reaction being[1990]:

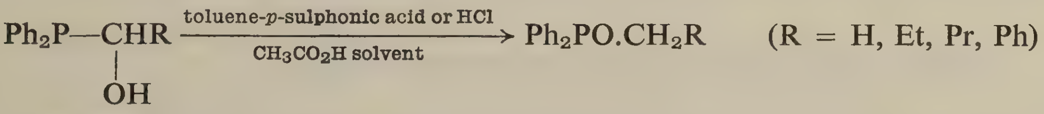
$$R_3P + CNCH(Br)CONH_2 + ROH \rightarrow R_3PO + RBr + CNCH_2CONH_2$$

Hydrolysis of tris-(trifluoromethyl)dichlorophosphorane gives an intermediate pentavalent hydrolysis product of unique structure, namely $(CF_3)_3POH.Cl$.[1963]

Esters of phosphinous acids undergo the Arbuzov reaction (pp. 1006, 1007) when heated with alkyl halide[1919] or alone:

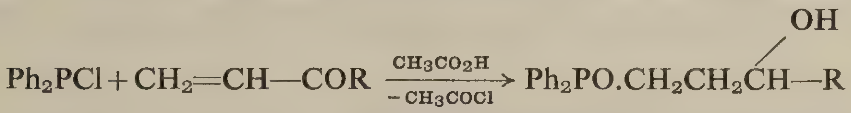
$$R_2P-OR' + R''X \rightarrow R_2PO.R'' + R'X$$

α-Hydroxyalkyldiphenylphosphines rearrange to alkyldiphenylphosphine oxides under strongly acidic conditions[1910, 1961]:

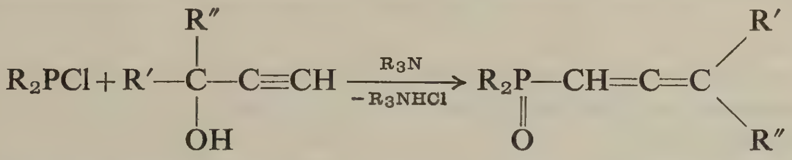


$$Ph_2P-\underset{\underset{OH}{|}}{C}HR \xrightarrow[CH_3CO_2H\ \text{solvent}]{\text{toluene-}p\text{-sulphonic acid or HCl}} Ph_2PO.CH_2R \qquad (R = H, Et, Pr, Ph)$$

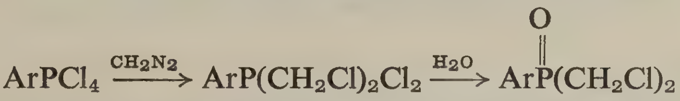
Diphenylphosphinyl chloride reacts with aldehydes and α-β unsaturated ketones giving α- and γ-hydroxysubstituted diphenylphosphine oxides respectively[451]:



Tertiary phosphine oxides having allenic substituents are formed from phosphinous halide and α-acetylenic alcohols in the presence of a base[791]:

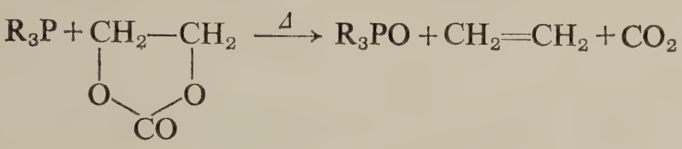


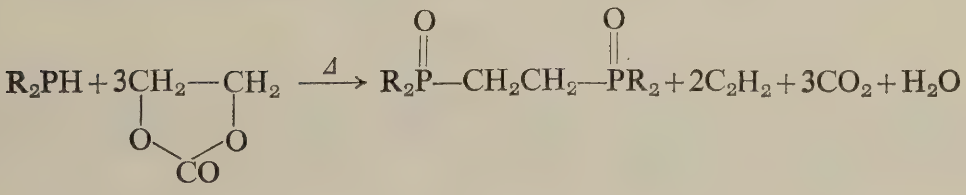
Chloromethylsubstituted phosphine oxides can be obtained from diazomethane and phosphorus pentachloride or aryltetrachlorophosphoranes[535]:

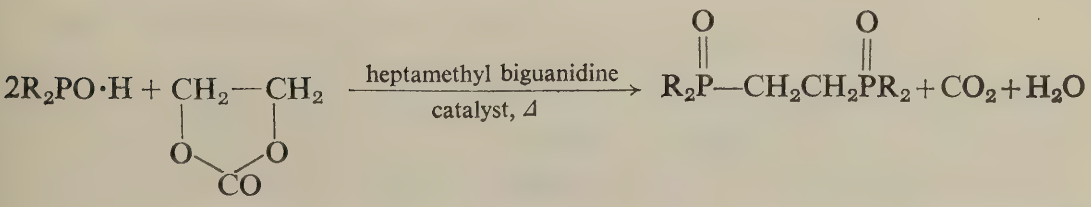


$$ArPCl_4 \xrightarrow{CH_2N_2} ArP(CH_2Cl)_2Cl_2 \xrightarrow{H_2O} Ar\overset{\overset{O}{\|}}{P}(CH_2Cl)_2$$

Ethylene and substituted ethylene carbonates react with tertiary phosphines, alone or with copper powder catalyst, giving tertiary phosphine oxide and the olefine corresponding to the carbonate used.[1984] Secondary phosphines and secondary phosphine oxides are converted to ethylenebisphosphine oxides or 2-hydroxyalkylphosphine oxides depending on the choice of the carbonate, catalyst, and reaction conditions[1983–4]:







Unsymmetrical phosphine oxides are conveniently obtained by the addition of alkyl halides to the reaction product of dialkyl phosphite and Grignard reagents[2053–4]:

$$(RO)_2PO.H + 3RMgX \rightarrow R_2PO.MgX + RH + 2ROMgX$$
$$R_2PO.MgX + R'X \rightarrow R_2R'PO + MgX_2$$

Phosphinous chlorides form phosphonium-like solid addition compounds with reactive alkyl halides such as α-chloroethers, α-chlorosulphides and benzyl chloride but do not react with simple alkyl chlorides. The complexes are decomposed on treatment with an alcohol and a base to form tertiary phosphine oxide and with hydrogen sulphide to form tertiary phosphine sulphide[2423–6]:

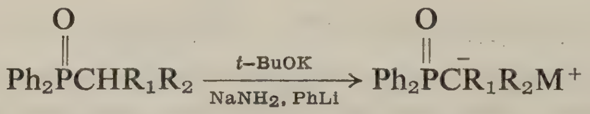
$$Et_2PCl + ClCH_2SEt \rightarrow [Et_2P(Cl)CH_2SEt]^+Cl^- \rightarrow \left[\begin{array}{l} \xrightarrow{EtOH} Et_2P(O)CH_2SEt \\ \xrightarrow{H_2S} Et_2P(S)CH_2SEt \end{array}\right.$$

1,2-Dichloroethyl ethers afford 1-alkoxyvinylphosphine sulphides:

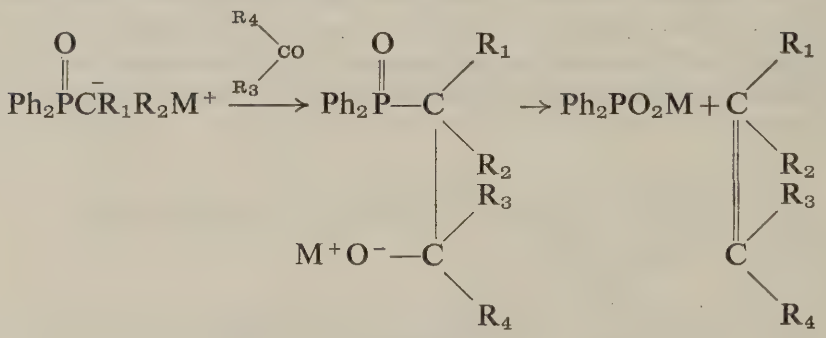
$$Ph_2PCl + BuOCH(Cl)CH_2Cl \rightarrow [\text{complex}] \xrightarrow{H_2S} Ph_2P(S)CH(OBu){=}CH_2$$

SOME REACTIONS OF TERTIARY PHOSPHINE OXIDES

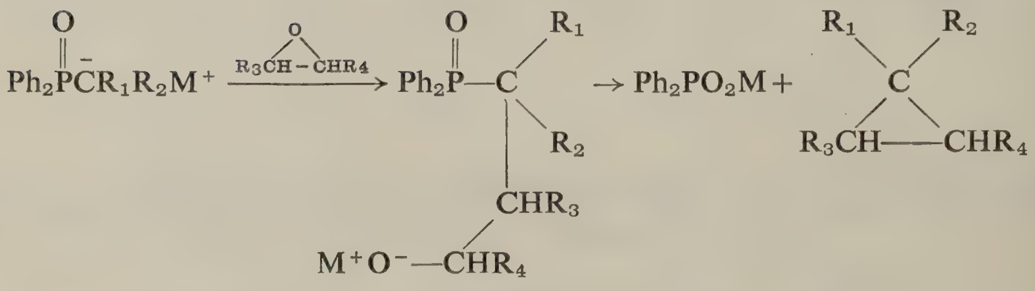
In a variation of the well-known Wittig reaction (p. 946), Horner and co-workers[1916, 1970–1] showed that phosphine oxide anions, formed by reaction of a phosphine oxide having at least one α-hydrogen atom with potassium *tert*-butoxide or $NaNH_2$, would react with aldehydes to form intermediates which decompose to phosphinate anion and olefine; reaction with epoxides leads to the formation of *cyclo*propane derivatives.[1976] When lithium salts of the phosphine oxide anion are used the intermediates (**XLV** and **XLVI**, M = Li) do not eliminate phosphinate anion, and the products isolated from the carbonyl or epoxide reaction after hydrolysis are β-hydroxy and γ-hydroxy phosphine oxide respectively:



$$Ph_2\overset{O}{\overset{\|}{P}}CHR_1R_2 \xrightarrow[NaNH_2,\ PhLi]{t\text{-}BuOK} Ph_2\overset{O}{\overset{\|}{P}}\bar{C}R_1R_2M^+ \qquad (M = Li, Na, K)$$

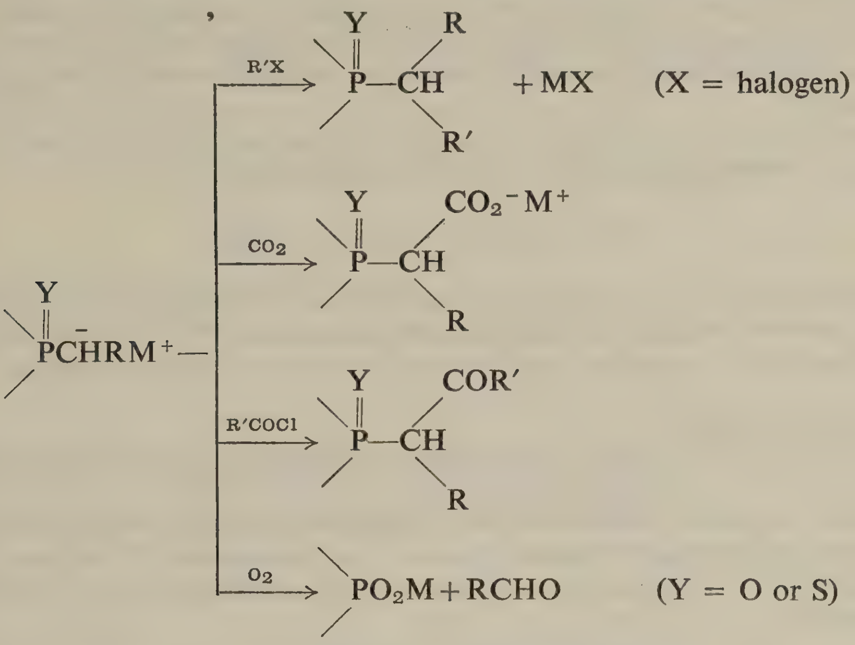


**XLV**



**XLVI**

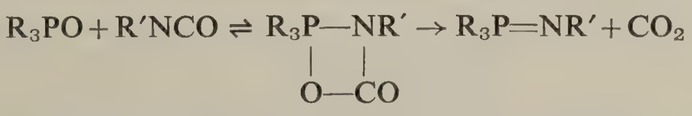
Salts of phosphine oxide/sulphide anions undergo many reactions which are typical of organoalkali compounds, introducing a new substituent (e.g., alkyl,[1928] carboxyl,[1981] acyl[1970-1]) on the $\alpha$-carbon atom; reaction with oxygen causes P–C bond fission to give a phosphinate anion and a carbonyl compound[1916]:



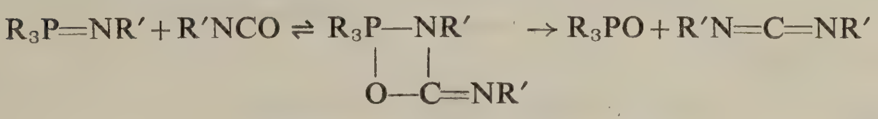
Triphenylphosphine oxide or sulphide and organo-alkali compounds such as benzylsodium,[1928] benzyllithium[1979-80] or methyllithium[1981] undergo rapid exchange followed by a slower but still rapid metalation to form $\alpha$-metallated alkyldiphenylphosphine oxide/sulphide, e.g.,

$$Ph_3PO + RCH_2Li \rightarrow Ph_2PO.CH_2R + PhLi$$
$$Ph_2PO.CH_2R + PhLi \rightarrow Ph_2PO.CHRLi + PhH$$

A number of phosphoryl compounds, phosphine oxides, phosphate esters, and phosphoramidates act as catalysts for the conversion of organic isocyanates and even isothiocyanates to carbodi-imides.[236-7,1878] The best catalysts are tertiary phosphine oxides, the most efficient of these being phospholene oxides such as 1-ethyl-3-methyl-3-phospholene-1-oxide[237,1904,1912] which is effective at a level of 0·1 part by weight of the isocyanate. The proposed catalytic process is indicated below[1878,1893]:



$$R_3PO + R'NCO \rightleftharpoons \underset{\displaystyle |\quad\ \ |\atop \displaystyle O—CO}{R_3P—NR'} \rightarrow R_3P{=}NR' + CO_2$$



$$R_3P{=}NR' + R'NCO \rightleftharpoons \underset{\displaystyle |\quad\ \ |\atop \displaystyle O—C{=}NR'}{R_3P—NR'} \rightarrow R_3PO + R'N{=}C{=}NR'$$

Tertiary phosphines and phosphine sulphides exert a similar catalytic effect and are converted during the reaction to the corresponding tertiary phosphine oxide.[236,1749,1904]

### Tertiary Phosphine Sulphides, Selenides and Tellurides

Tertiary phosphine sulphides and selenides are generally prepared by the direct addition of elemental sulphur or selenium to the corresponding tertiary phosphine under an atmosphere of nitrogen and generally in an inert solvent.[1,2,133,141,200,1779] The reaction of triarylphosphines with sulphur has been studied kinetically[132,135-7];

in benzene solution the reaction of triphenylphosphine with $S_8$ is slow and is believed to proceed by an initial nucleophilic attack by triphenylphosphine on the $S_8$ ring; the reaction rate is strongly accelerated by small amounts of phenol, methanol or acetonitrile. Other forms of sulphur, e.g., $S_2$, react very rapidly with triphenylphosphine. Triphenylphosphine is readily converted to triphenylphosphine sulphide by reaction with organic disulphides,[123, 259, 261] tetrasulphides,[260] diacoyl disulphides or bis(*O*,*O*-dialkylthiophosphoryl)disulphides; dibenzoyl disulphide is reported to be unreactive.[1]

Tertiary phosphine selenides are conveniently obtained from potassium selenocyanate and tertiary phosphine in acetonitrile solution[2334]:

$$R_3P + KSeCN \rightarrow R_3PSe + KCN$$

Few tertiary phosphine tellurides are reported; they are made by direct combination in boiling toluene solution under a nitrogen atmosphere.[140, 2349] The compounds are pale golden-yellow crystalline solids which deposit tellurium on storage:

$$RR'_2P + Te \rightarrow RR'_2PTe$$

$$(R,R' = \text{Et, Bu, Pr or cyclohexyl; if } R = \text{Ph}, R' = \text{Pr or Bu})$$

Phosphorus pentasulphide reacts with Grignard reagents giving many products; a large excess of Grignard reagent favours the formation of tertiary phosphine sulphides.[134, 1764] Thiophosphoryl chloride may be alkylated using organolithium compounds[200]:

$$3MeLi + PSCl_3 \rightarrow Me_3PS + 3LiCl$$

The aluminium halide catalysed reaction of a thiophosphoryl chloride or bromide with benzene affords a mixture of phenylphosphonothionic dihalide, diphenylphosphinothionic halide, and triphenylphosphine sulphide, the proportions of which depend on the proportions of reagents used. Unsymmetrical tertiary phosphines may be obtained by starting with the appropriate phosphonothionic dihalide or phosphinothionic halide[1749]:

$$PSCl_3 + AlCl_3 + PhH(\text{excess}) \xrightarrow[\text{reflux}]{\text{8 hours}} Ph_3PS(85\%) + Ph_2PSCl + PhPSCl_2$$
$$RPSBr_2 + AlBr_3 + PhH \rightarrow Ph_2PS.R$$
$$R_1R_2PSBr + AlBr_3 + PhH \rightarrow PhPS.R_1R_2$$

Some reactions of tertiary phosphine sulphides are shown in Chart V.

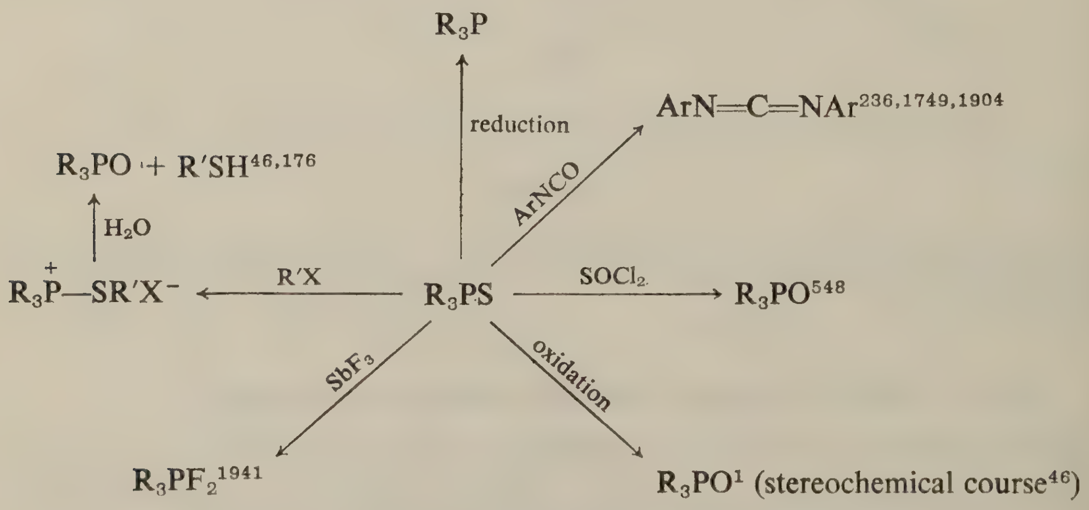
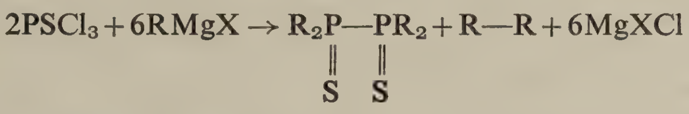


CHART V.—Reactions of tertiary phosphine sulphides

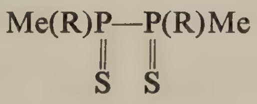
### Diphosphine Disulphides

In 1949 Kabachnik and Shepeleva[1931] showed that the reaction of thiophosphoryl chloride with methyl magnesium bromide formed, not the expected trimethylphosphine sulphide, but a new class of compound, tetramethyldiphosphine disulphide, $Me_2PS–PSMe_2$, in good yield. The generality of this reaction, which for some years was considered anomalous, has been demonstrated by several groups of workers in recent years.[25, 30, 34, 68, 323, 1885, 1903, 1933–4] Yields of up to 90% of tetra-alkyldiphosphine disulphide are reported[30] from the reaction:



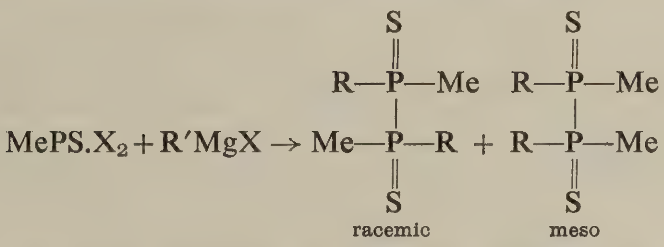
$$2PSCl_3 + 6RMgX \rightarrow \underset{\underset{S}{\|}}{R_2P}—\underset{\underset{S}{\|}}{PR_2} + R—R + 6MgXCl$$

Symmetrical disulphides of the type



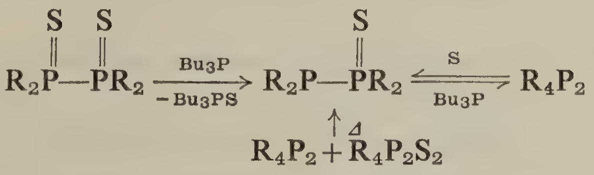
$$\underset{\underset{S}{\|}}{Me(R)P}—\underset{\underset{S}{\|}}{P(R)Me}$$

(where R = ethyl, propyl, butyl, hexyl, and benzyl) have been obtained by the action of the appropriate Grignard reagent on methylphosphorothionodihalides, and were shown to exist in both racemic and meso forms[323, 1935, 2422]:



$$MePS.X_2 + R'MgX \rightarrow \begin{array}{c} S \\ \| \\ R—P—Me \\ | \\ Me—P—R \\ \| \\ S \\ \text{racemic} \end{array} + \begin{array}{c} S \\ \| \\ R—P—Me \\ | \\ R—P—Me \\ \| \\ S \\ \text{meso} \end{array}$$

Tetra-alkyldiphosphine monosulphides have been prepared by the partial reduction of the disulphides with tributylphosphine, by partial sulphuration of tetra-alkyldiphosphine and by equilibration of a diphosphine with the corresponding diphosphine disulphide[323, 1888–9, 1937]:



$$\overset{\overset{S}{\|}}{R_2P}—\overset{\overset{S}{\|}}{PR_2} \xrightarrow[-Bu_3PS]{Bu_3P} R_2P—\overset{\overset{S}{\|}}{PR_2} \underset{Bu_3P}{\overset{S}{\rightleftharpoons}} R_4P_2$$

$$\uparrow \Delta$$

$$R_4P_2 + R_4P_2S_2$$

Tetra-alkyldiphosphine disulphides have proved to be extremely versatile intermediates for the preparation of dialkyl substituted organophosphorus compounds in good yields. Reactions are indicated in Chart VI.

Acetylenic Grignard reagents are reported to react normally with thiophosphoryl chloride to form trialkynylphosphine sulphides.[2335]

## PHOSPHONIUM COMPOUNDS

These compounds have the general formula $R_1R_2R_3R_4P^+X^-$, where $R_1$, etc., represent organic radicals bonded to the phosphorus atom by a P–C bond and X is an acid radical.

### Preparation

#### REACTION OF TERTIARY PHOSPHINES WITH ALKYL HALIDES

The simplest and most widely used method of preparing quaternary phosphonium halides is the reaction of tertiary phosphines with alkyl halides.[1, 2004] Polar solvents

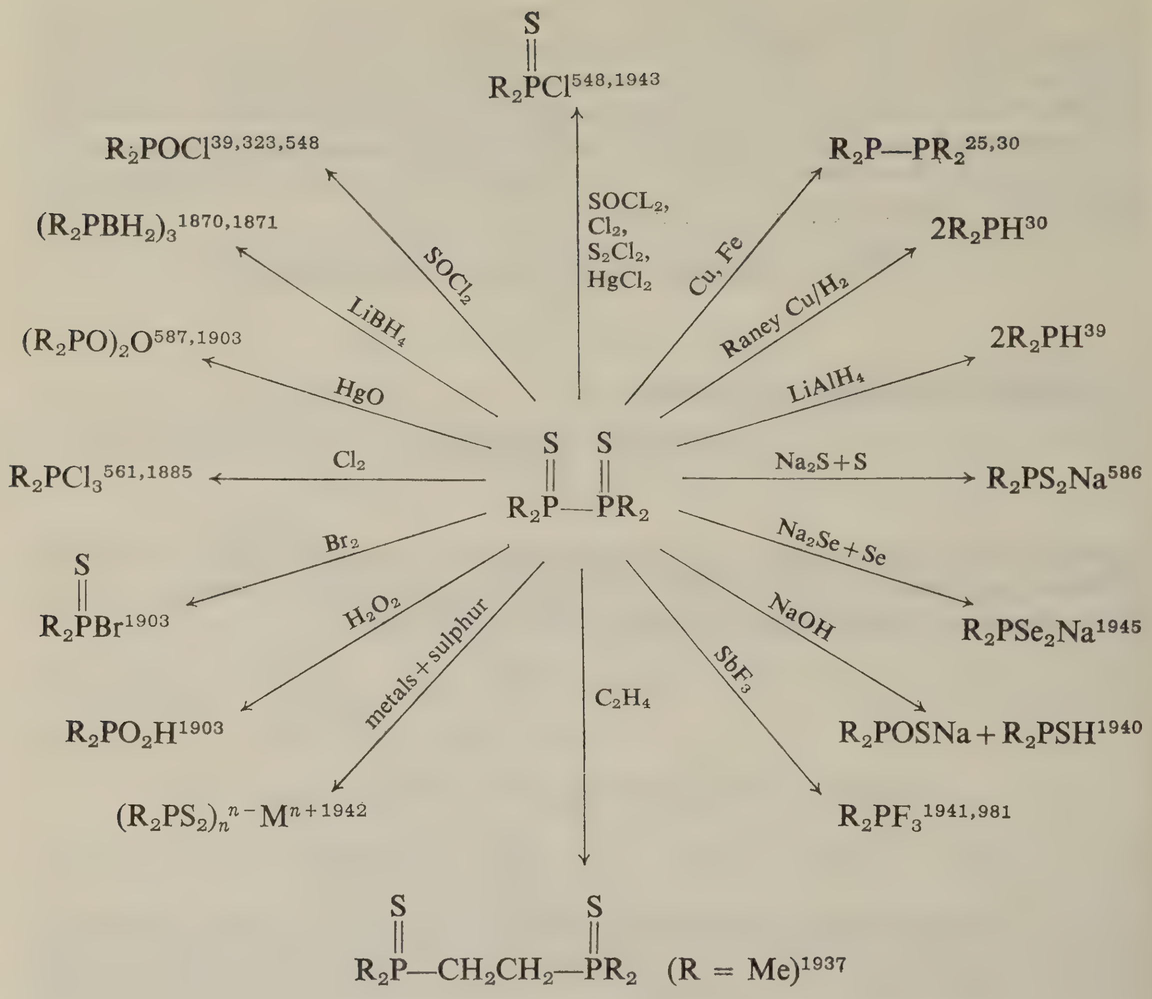


CHART VI.—Reactions of tetra-alkyl diphosphine disulphides

such as acetonitrile, formic acid and nitromethane are frequently used to facilitate reaction[41]:

$$R_1R_2R_3P + R_4X \rightarrow R_1R_2R_3R_4P^+X^-$$

Studies of the reaction show that the reaction rate decreases rather rapidly with increasing bulk of both constituents and, unlike the basicity of phosphines, is affected by steric and conjugative effects as well as by polar factors. Early work showed that in reactions of alkyl halides with phosphines of the type $ArPEt_2$ in acetone solution[1748] the reaction rates are faster, and the effect of substituents in the aryl ring is less than in the corresponding arsines and amines, $ArAsEt_2$ and $ArNEt_2$ respectively. The effect of substituents in the *para*-position of the benzene ring on the reaction rate was:

methoxy > methyl > hydrogen > phenoxy > chlorine > bromine

More recently the nucleophilic order of a number of secondary and tertiary phosphines has been determined from the kinetics of the reaction of the phosphines with ethyl iodide in acetone solution[1739]:

$$R_3P + EtI \rightarrow R_3\overset{+}{P}EtI^-$$
$$R_2PH + EtI \rightarrow R_2\overset{+}{P}HEtI^-$$

The reactions were bimolecular and the reaction rates of various phosphines decreased in the order: trialkyl > $PhPEt_2 > Ph_2PEt > (p\text{-}CH_3OC_6H_4)_3P > (alkyl)_2PH > Ph_3P > (CNCH_2CH_2)_3P$. The reaction rates in this series varied by a factor of more than $10^3$. For a number of phosphines, e.g., trialkyl-, triaryl- and arylethylphosphines, the reaction rate, $k$, could be expressed in the form of an equation:

$$\log_{10} k = a - b \sum \sigma^*$$

where $\sum \sigma^*$ is the sum of the Taft values for the substituted groups of the phosphine and $a$ and $b$ are constants. Thus, for these phosphines, the nucleophilic character, like the basicity, is determined largely by the inductive effect as measured by $\sum \sigma^*$. The reaction rates of phosphines which contain one or more methyl groups, tri-*iso*butylphosphine, and tris-(2-cyanoethyl)phosphine deviated from the above equation by amounts sufficient to indicate the operation of steric and/or conjugative effects.

The relative reactivities of various primary alkyl iodides with tri-*n*-butylphosphine in acetone are similar to those found on varying the substituent in other $S_N2$ reactions.[2007] The reactions proceed faster in polar than in non-polar solvents.[1739, 1748] Relative reaction rates of *n*-propyl halides with tri-*n*-butylphosphine are I:Br:Cl = 2660:248:1.[1739] The enthalpy and entropy of activation of tributyl- and triphenylphosphine with ethyl iodide in acetone are 12·5 ± 0·1, 14·2 ± 0·1 kcal./mole and −31 ± 1, −33 ± 1 e.u. respectively.[1739]

$\alpha$-$\omega$-Primary dihalides generally react normally with tertiary phosphines to form bis-quaternary phosphonium salts. Methylene dihalides can react anomalously (see p. 934). Quaternization of tertiary phosphines, e.g., triphenylphosphine with secondary and tertiary alkyl halides, is complicated by olefine formation.[1998] Triphenyl-*tert*-butylphosphonium chloride has been obtained by heating triphenylphosphine with an excess of *tert*-butyl chloride in formic acid at 130° under pressure.[41] When the reaction is conducted under reflux the products are triphenylphosphine hydrochloride and 2-methylpropene.[1998]

Allylic rearrangement occurs in the reaction of triphenylphosphine with 1-bromo-2-methylene*cyclo*hexyl compounds.[1997]

### THE REACTION OF PHOSPHINES WITH CARBONYL COMPOUNDS

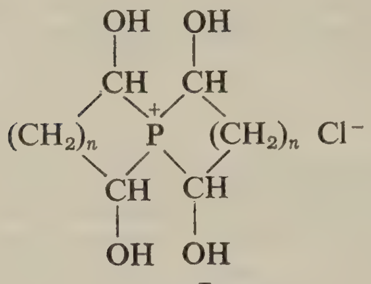
Early work in this field showed that aliphatic aldehydes and $\alpha$-chloroaldehydes condense with phosphonium iodide[1720] or with phosphine in ether solution in the presence of hydrochloric or hydrobromic acid catalyst.[1706] Crystalline tetrakis-($\alpha$-hydroxyalkyl)-phosphonium salts were isolated from the lower aliphatic aldehydes.

Phosphine[273–4, 832] and substituted phosphines[275–7, 279, 282, 1290, 1784] react in concentrated aqueous hydrochloric acid with aqueous formaldehyde to give excellent yields of hydroxymethylphosphonium chlorides:

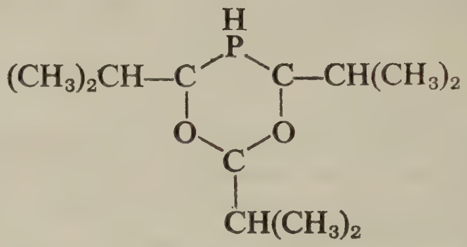
$$PH_3 + 4CH_2O + HCl \rightarrow (HOCH_2)_4\overset{+}{P}Cl^-$$
$$PhPH_2 + 3CH_2O + HCl \rightarrow Ph\overset{+}{P}(CH_2OH)_3Cl^-$$
$$Bu_2PH + 2CH_2O + HCl \rightarrow Bu_2\overset{+}{P}(CH_2OH)_2Cl^-$$
$$Ph_3P + CH_2O + HCl \rightarrow Ph_3\overset{+}{P}CH_2OHCl^-$$

Under similar conditions phosphine and *n*-alkyl aldehydes form tetrakis-($\alpha$-hydroxyalkyl)-phosphonium chlorides[1300, 2073] while dialdehydes which can form relatively stable 5- or 6-membered rings, such as succindialdehyde and glutaraldehyde, form spirocyclic phosphonium compounds **I**.[856, 1300] Secondary phosphines react with these dialdehydes giving monocyclic phosphonium salts.[575, 1034] $\alpha$-Branched aldehydes and phosphine form novel heterocyclic compounds, e.g., *iso*butyraldehyde gives

2,4,6-tri-*iso*propyl-1,3-dioxa-5-phosphine, **II**.[856, 1300] Chloral forms bis-(2,2,2-trichloro-1-hydroxyethyl)phosphine.[1300, 2124]



**I**



**II**

Benzaldehyde has been reported to react with phosphine in a mixture of concentrated hydrochloric acid and an alcohol to give tris- and bis-(α-alkoxybenzyl)phosphine.[2070, 2123–4] In concentrated hydrochloric acid solution and in organic solutions of hydrochloric acid the products are bis-(α-hydroxybenzyl)-benzylphosphine oxides[1290, 2123]:

$$3ArCHO + PH_3 \xrightarrow{H^+} (ArCHOH)_2PO.CH_2Ar$$

Phosphine and formaldehyde solution readily form trishydroxymethylphosphine in the presence of many metal salts[1284]; similar catalyzed reactions are reported for acetaldehyde, crotonaldehyde, butyraldehyde, glyoxal and chloroacetaldehyde[2119]:

$$PH_3 + 3RCHO \xrightarrow{PtCl_4} (RCHOH)_3P$$

Primary and secondary phosphines such as phenylphosphine and dibutylphosphine will form the hydroxymethyl tertiary phosphine by reaction with commercial formalin solution without added catalyst.[280, 282, 1217] At 100° phosphine, primary and secondary alkyl phosphines react with paraformaldehyde giving similar products[1268, 2318]:

$$RPH_2 \rightarrow RP(CH_2OH)_2$$
$$R_2PH \rightarrow R_2PCH_2OH$$

Kinetics and activation energies for the reaction of $PH_3$, $MePH_2$, $EtPH_2$ and MeEtPH with paraformaldehyde have been evaluated.[1237] Phosphine and aqueous formaldehyde are reported to form tetrakis-(hydroxymethyl)phosphonium hydroxide.[1257]

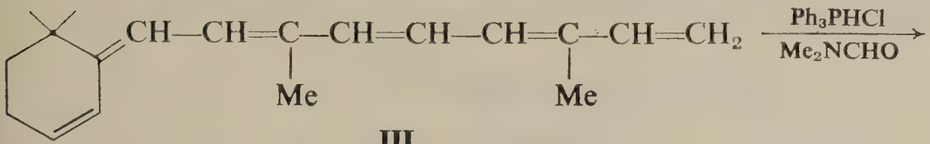
Primary phosphines and dienones react by addition of the phosphine to the C=C double bond rather than to the carbonyl group to form 4-phosphorinanones.[2072] Hexafluoroacetone and phosphine readily form $(CF_3)_2CH(OH)PH_2$ at 60° but acetone and phosphine fail to react at 100°.[2340] The reactions of phosphines with carbonyl compounds have been reviewed.[1909–10]

### ADDITION OF TERTIARY PHOSPHINES TO OLEFINS

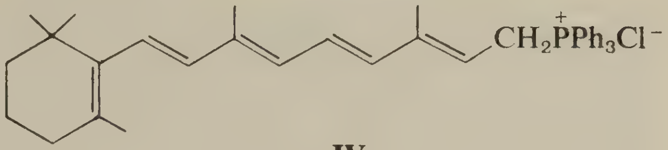
Sarnecki and Pommer[2014–5] have shown that phosphonium salts may be obtained by the action of triphenylphosphonium halides (preferably the bromide) on alcohols:

$$2Ph_3\overset{+}{P}HBr^- + HO(CH_2)_4OH \rightarrow Ph_3\overset{+}{P}(CH_2)_4\overset{+}{P}Ph_3Br_2{}^-$$

Triphenylphosphonium salts add $\alpha$–$\omega$ to conjugated olefins; for example, the hexaene **III** adds triphenylphosphonium chloride to give the phosphonium salt **IV.**[2015]

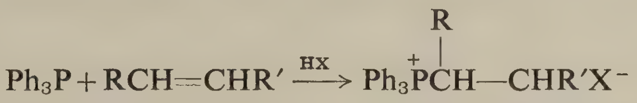


**III**



**IV**

Phosphonium salts have also been prepared by the addition of triphenylphosphine to compounds having a polarized carbon–carbon double bond[2010]:



$$Ph_3P + RCH{=}CHR' \xrightarrow{HX} Ph_3\overset{+}{P}\overset{\overset{R}{|}}{C}H{-}CHR'X^-$$

$$(R = H, Me, Ph, CO_2H, CO_2R;\ R' = CO_2H, CO_2Et, CONH_2, CN, NO_2)$$

Trishydroxymethylphosphine and acrylic acid form $\beta$-(trishydroxymethylphosphonio)propionic acid $\beta$-lactone[2017]:

$$(HOCH_2)_3P + CH_2{=}CHCO_2H \rightarrow (HOCH_2)_3\overset{+}{P}CH_2CH_2CO_2^-$$

ADDITIONS TO ALKYLIDENEPHOSPHORANES

Alkylidenephosphoranes add halogen acids to form phosphonium halides[2018, 2021] and add halogens to form $\alpha$-halogenoalkylphosphonium halides[2024, 2026–7]:

$$Ph_3P{=}CH_2 + XBr \rightarrow Ph_3\overset{+}{P}{-}CH_2XBr^- \qquad (X = H, Br)$$

Alkyl halides effect $\alpha$-carbon alkylation[2024] affording a valuable route to secondary and tertiary alkyl-substituted phosphonium salts. Thus, *iso*propyltriphenylphosphonium iodide may be converted to *tert*-butyltriphenylphosphonium iodide[2016]:

$$Ph_3\overset{+}{P}CHMe_2I^- \xrightarrow{BuLi} Ph_3P{=}CMe_2 \xrightarrow{MeI} Ph_3\overset{+}{P}CMe_3I^-$$

Acyl halides and alkylidenephosphoranes form a mixture of phosphonium salt and acylated phosphorane, the overall reaction being [2012]:

$$2Ph_3P{=}CHR + RCOCl \rightarrow Ph_3P{=}CR.CO.R + Ph_3\overset{+}{P}CH_2RCl^-$$

Many metallic and non-metallic halides (e.g., $HgBr_2$, $Me_3SiBr$, $Ph_3GeBr$, $Me_3SnBr$, $Me_2SnBr_2$, $Ph_2PBr$, $PhPBr_2$) have been shown to react with alkylidenephosphoranes forming phosphonium salts in which the respective hetero-atom is linked to phosphorus through a methylene group[2022–3, 2341, 2427]:

$$Ph_3P{=}CH_2 + Me_3SiBr \rightarrow Ph_3\overset{+}{P}CH_2SiMe_3Br^-$$

$$2Ph_3P{=}CH_2 + PhPBr_2 \rightarrow (Ph_3\overset{+}{P}CH_2)_2PPhBr_2^-$$

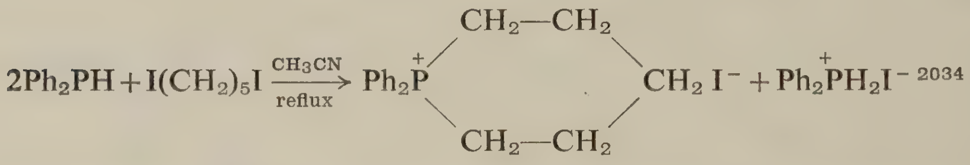
Boron compounds (hydrides, halides and triphenyl boron) give adducts which may be represented formally as zwitter-ionic phosphonium salts[2020, 2022]:

$$Ph_3P{=}CH_2 \xrightarrow{B_2H_6} Ph_3\overset{+}{P}{-}CH_2BH_3^-$$

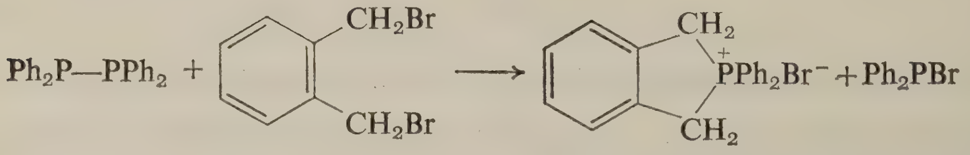
MISCELLANEOUS REACTIONS

Phosphonium salts are formed when phosphonium iodide, primary or secondary phosphines, metal phosphides, halogenophosphines and halogenophosphoranes are heated with alkyl halides:

$$EtPLi_2 + MeI \rightarrow Et\overset{+}{P}Me_3I^{-}\ ^{24}$$



Tetraphenyldiphosphine undergoes P–P bond fission when heated with alkyl halides to form a mixture of diphenylalkylphosphine, which is further alkylated to a diphenyldialkylphosphonium halide, and a diphenylphosphinyl halide.[2037] A novel route to diphenyl cyclic phosphonium salts involves reaction of the diphosphine with $\alpha$-$\delta$ dibromides such as 1,4-dibromobutene-2 and 1,2-dibromomethyl benzene.[2036]



Tertiary phosphines quaternize with the lower alkyl and benzyltoluenesulphonic esters[2029] giving phosphonium tosylates, and with triethyloxonium fluoroborate[2038] or triethoxycarbonium fluoroborate[2030] giving phosphonium fluoroborates:

$$R_3P + R'OTs \rightarrow R_3R'\overset{+}{P}OTs^{-} \qquad (Ts = p\text{-}CH_3.C_6H_4SO_2\text{–})$$
$$PhP(CH_2Cl)_2 + Et_3\overset{+}{O}BF_4^{-} \rightarrow PhEt\overset{+}{P}(CH_2Cl)_2BF_4^{-} + Et_2O$$
$$R_3P + (EtO)_3\overset{+}{C}BF_4^{-} \rightarrow EtR_3\overset{+}{P}BF_4^{-} + (EtO)_2CO \qquad (R = Et, Ph)$$

The reaction of quaternary ammonium salts of Mannich bases,[2031] and of aromatic carbonium ion salts[2030, 2342] with tertiary phosphines affords a route to many phosphonium salts which are difficult to obtain by other methods:

$$Ph_3P + RCH_2NMe_3X \rightarrow Ph_3\overset{+}{P}CH_2RX^{-} + Me_3N$$
$$Ph_3P + Ar_2\overset{+}{C}OEt.BF_4^{-} \rightarrow Ar_2C(OEt)\overset{+}{P}Ph_3.BF_4^{-} \qquad (Ar = p\text{-}MeOC_6H_4CH{=}CH\text{—})$$

Trishydroxymethylphosphine and epoxides react readily in the absence of acids to form strongly basic phosphonium hydroxides; with acids the product is a 2-hydroxyalkyltrishydroxymethylphosphonium salt.[2032] The same phosphine and *N*-methylolurea afford ureidomethyltrishydroxymethylphosphonium hydroxide which can be isolated as the picrolonate salt[2033]:

$$P(CH_2OH)_3 + NH_2CONHCH_2OH \xrightarrow{50^\circ} NH_2CONHCH_2\overset{+}{P}(CH_2OH)_3OH^{-}$$

Low yields of phosphonium salts have been obtained by the cuprous halide catalyzed decomposition of aliphatic diazonium compounds in the presence of tertiary phosphines and acids.[2035]

The conditions under which methyl chloride or methyl bromide and white phosphorus react to form high yields of tetramethylphosphonium halides have been established.[2343]

## THE REACTION OF PHOSPHINES WITH ORGANIC COMPOUNDS CONTAINING A HIGHLY REACTIVE (POSITIVE) HALOGEN ATOM

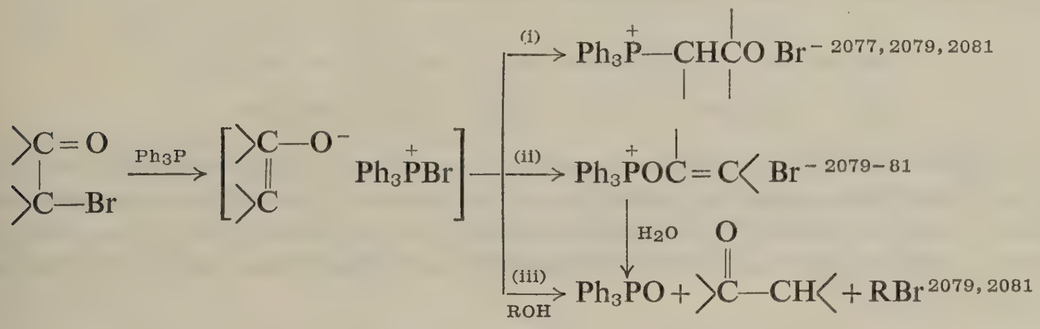
Trivalent phosphorus compounds and simple primary alkyl halides generally react by nucleophilic attack of phosphorus on carbon to form a P–C bond:

$$>P + >C—X \rightarrow >\overset{+}{P}—C< + X^-$$

In recent years a considerable amount of evidence has accumulated which indicates that with a highly reactive (positive) halogen compound the initial nucleophilic attack by phosphorus can occur on the halogen atom to form a halogenophosphonium or halogenoquasiphosphonium ion-pair intermediate which undergoes further reactions to give the ultimate reaction products (see reviews by Hoffmann & Diehr[2075] and Miller[2076]):

$$>P + X—Y \rightarrow \left[>\overset{+}{P}—X.Y^-\right] \rightarrow \text{Products}$$

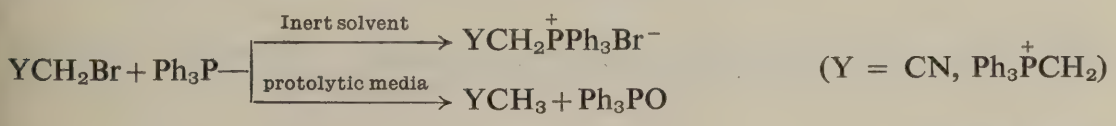
The ultimate fate of halogenophosphonium carbanion ion-pairs derived from tertiary phosphines and highly reactive (positive) halogen compounds (e.g., α-bromosulphones, α-bromonitriles, bromoacetylenes, α-bromoketones, halogenoamides and α-halogenoalkylphosphonium salts) depends on the reaction medium and the structure of the halogen compound. In inert media the ion pair can rearrange to form a normal phosphonium salt (route i) or, if the anion is mesomeric, to form an isomeric quasiphosphonium compound (route ii). In protolytic media the ultimate products are tertiary phosphine oxide and a reduced halogen compound (route iii). All three types of reaction have been observed in the reaction of triphenylphosphine with α-halogenoketones and are illustrated below:



Recombination of the intermediate phosphonium-enolate ion-pair according to either route (i) or (ii) has been shown to be determined by the frontier electron densities (cf. Fukui *et al.*[2434]) of the carbon and oxygen atoms in the enolate ion.[2083]

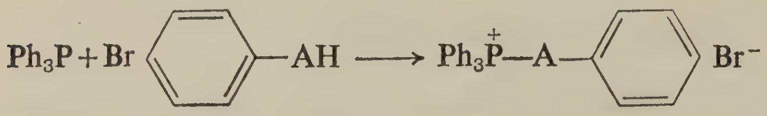
Enol phosphonium salts formed by the reaction of triphenylphosphine with chloral[2080] and α-halogenoketones such as α-bromo*cyclo*hexanone[2079, 2083] and $Ph_2CCl.CO.Ph$[2082] are extremely hygroscopic. They are rapidly decomposed by water, alcohol and protolytic reagents.

Two well-established examples of the effect of solvent on the ultimate reaction products are the reactions of bromoacetonitrile and bromoethyltriphenylphosphonium bromide with triphenylphosphine. In inert media the products are cyanomethyltriphenylphosphonium bromide[2084] and methylenebis(triphenylphosphonium) dibromide[2028] respectively. In protolytic media the solvents and products are respectively: moist chloroform, methyl cyanide[2084]; methanol, triphenylmethylphosphonium bromide,[2085] together with triphenylphosphine oxide:



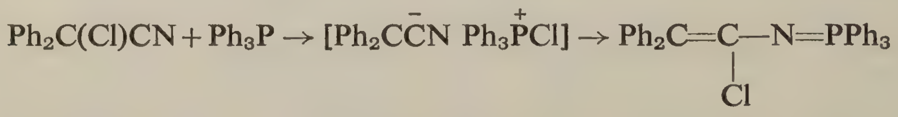
$$YCH_2Br + Ph_3P — \begin{cases} \xrightarrow{\text{Inert solvent}} YCH_2\overset{+}{P}Ph_3Br^- \\ \xrightarrow{\text{protolytic media}} YCH_3 + Ph_3PO \end{cases} \qquad (Y = CN, Ph_3\overset{+}{P}CH_2)$$

*ortho-* and *para*-Bromo-aromatic amines and phenols react with triphenylphosphine to form phosphinimidium salts (*N*-quasiphosphonium salts) and aryloxytriphenylphosphonium salts respectively.[2088] Reaction of the amines is acid-catalyzed and is inhibited by aliphatic amines.[2089]



(A = O or NH)

In the reaction of triphenylphosphine with chlorodiphenyl acetonitrile in the absence of a protic solvent the initially formed ion-pair forms a halogenovinyl phosphine imine.[2252–3] In the presence of water the products are triphenylphosphine oxide, diphenylacetonitrile and hydrogen chloride.



$$Ph_2C(Cl)CN + Ph_3P \rightarrow [Ph_2C\overset{-}{C}N\ Ph_3\overset{+}{P}Cl] \rightarrow Ph_2C{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}N{=}PPh_3$$

$$Ph_2C(Cl)CN + Ph_3P \rightarrow [Ph_2C\overset{-}{C}N\ Ph_3\overset{+}{P}Cl] \xrightarrow{H_2O} Ph_2CHCN + Ph_3PO + HCl$$

### REACTION OF POLYHALOGENOMETHANES

In inert media triphenylphosphine and methylene dibromide form the expected methylenebis(triphenylphosphonium) dibromide.[2028] The reaction with bromoform is sluggish and proceeds readily only in the presence of a free-radical catalyst to form dibromomethyltriphenylphosphonium bromides.[2019, 2079] With carbon tetrachloride and carbon tetrabromide the final products are dihalogenomethylenetriphenylphosphorane and triphenyldihalogenophosphorane[2024–5]:

$$Ph_3P + CBr_4 \rightarrow [Ph_3\overset{+}{P}Br + CBr_3^-] \rightarrow [Ph_3\overset{+}{P}{-}CBr_3]Br^-$$
$$[Ph_3\overset{+}{P}{-}CBr_3]Br^- + Ph_3P \rightarrow Ph_3P{=}CBr_2 + Ph_3PBr_2$$

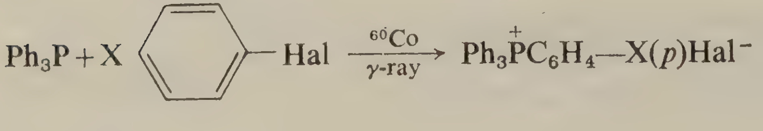
In alcoholic solution, bromoform and carbon tetrachloride afford high yields of triphenylphosphine oxide by hydrolysis of the initially formed halogenophosphonium-carbanion ion-pair.[2086] Trifluoroiodomethane and trimethylphosphine undergo a novel reaction giving tetramethylphosphonium iodide and trifluoromethyldimethylphosphine[2087]:

$$CF_3I + Me_3P \rightarrow [CF_3^-I\overset{+}{P}Me_3] \rightarrow Me_3\overset{+}{P}CF_3I^- \xrightarrow{Me_3P} Me_4\overset{+}{P}I^- + Me_2PCF_3$$

### ARYL PHOSPHONIUM COMPOUNDS

The thermally induced quaternization of triphenylphosphine with chlorobenzene and bromobenzene has not been realized. Moderate yields of tetra-arylphosphonium salts have been obtained by heating arylphosphines and aryl bromides in the presence of aluminium chloride,[1157, 2005] by ultra-violet light irradiation of mixtures of triphenylphosphine and aryl iodide in chlorobenzene solvent,[2006] and by $\gamma$-irradiation of mixtures of triphenylphosphine and aryl halides.[2337]

$$Ar_3P + ArBr \xrightarrow{AlCl_3} Ar_4\overset{+}{P}Br^- \qquad (Ar = p\text{-}/m\text{-}CH_3C_6H_4{-},\ C_6H_5)$$
$$Ph_3P + ArI \xrightarrow{uv} Ph_3\overset{+}{P}ArI^- \qquad (Ar = C_6H_5{-},\ p\text{-}HOC_6H_4{-})$$



(X = H, Cl, Br, $CH_3$)

Refs. p. 1082

Aryl polytriphenylphosphonium bromides are obtained by quaternization of di- and polyaryl bromides with triphenylphosphine in diethylene glycol diethyl ether solvent, e.g., 1,2,4,5-tetrabromobenzene gives benzene-1,2,4,5-tetrakis(triphenylphosphonium) tetrabromide.[1155, 1210]

Aromatic free-radicals, generated by the action of oxygen or cobalt chloride on Grignard reagents,[1106–7, 1071, 1113, 2339] by the decomposition of aryldiazonium salts and by the decomposition of arylnitrosodiazonium acetate,[1106, 1996] react with arylphosphines to give good yields of tetra-arylphosphonium salts:

$$\mathrm{Ph_3P + ArN_2Cl \xrightarrow[\text{buffer}]{\text{NaOAc}} Ph_3\overset{+}{P}ArCl^-}$$

$$\mathrm{Ph_3P + ArMgX \xrightarrow[\text{CoCl}_2]{\text{O}_2\text{ or}} Ph_3\overset{+}{P}ArX^-}$$

Dodonov and Medox showed that in the formation of $Ph_4PBr$ from triphenylphosphine and phenylmagnesium bromide in ether solution the yield was 13–14% in air, 72% in oxygen and only 5% in hydrogen.[1113]

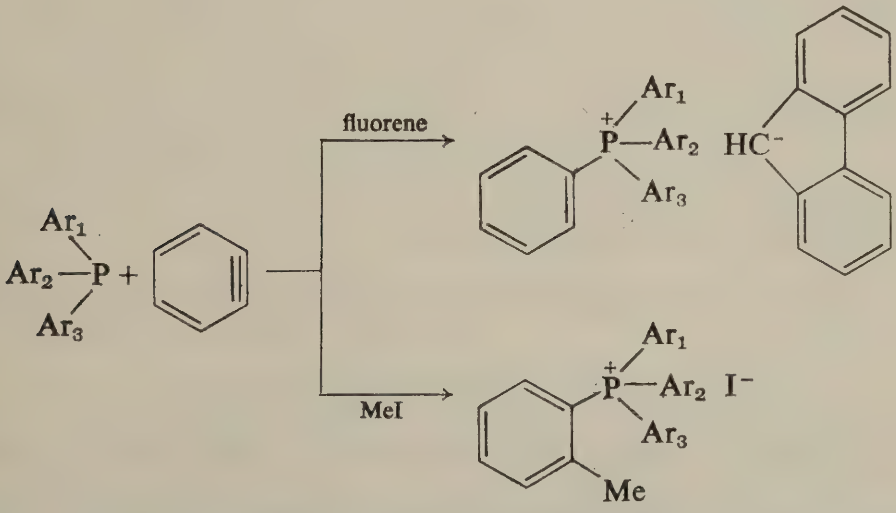
The photochemically or thermally induced reaction of diphenyliodonium chloride or borofluoride with triphenylphosphine in alcoholic media gives 40–50% yields of tetraphenylphosphonium chloride or borofluoride respectively.[2051–2, 2336]

Triarylphosphine complexes of cadmium and mercury halides, $(Ar_3P)_2MX_2$ ($M = Cd, Hg$; $X = Br, I$), react with alkyl bromides or iodides to form bis-(triarylalkylphosphonium)tetrahalogenometal compounds $[(Ar_3PR)^+]_2MX_4^{2-}$.[1754, 2428] This reaction has been extended by Horner and co-workers to the reaction of aryl halides with tertiary phosphine complexes of bromides and chlorides of $Ni^{II}$, $Co^{II}$, $Zn^{II}$, $Cu^{II}$, $Mn^{II}$ and $Fe^{II}$. The reactions are carried out in the melt or in boiling benzonitrile giving good yields of arylphosphonium salts[2338]:

$$\mathrm{2R_3P + MX_2 \xrightarrow{80^\circ} (R_3P)_2MX_2 \xrightarrow[120^\circ]{ArX} [R_3PAr]^+R_3P.MX_3^- \xrightarrow[180^\circ]{ArX} [(R_3PAr)^+]_2MX_4^{2-}}$$

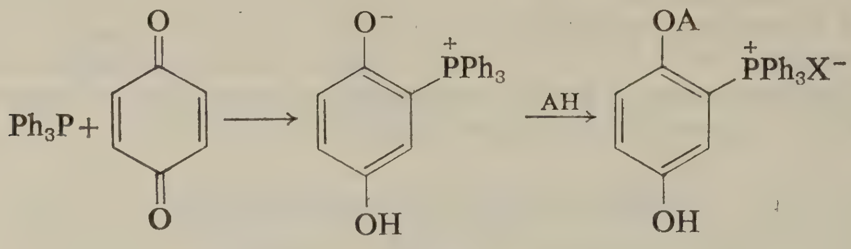
($R$ = alkyl, aryl; $X$ = Cl, Br; $M$ preferably Ni, Co)

Benzyne and triphenylphosphine give low yields of tetraphenylphosphonium salts.[298] At −40° in the presence of fluorene, arylphosphines and benzyne form tetra-arylphosphonium fluorenide from which phosphonium salts can be obtained in 67% yield by treatment with an acid. With methyl iodide[2009] or triphenyl boron[298] instead of fluorene the product is an *o*-substituted phenyltriphenylphosphonium compound:



($Ar_1 = Ar_2 = Ar_3 = Ph$; $Ar_1 = Ph$, $Ar_2 = p$-tolyl, $Ar_3 = p$-diphenyl)

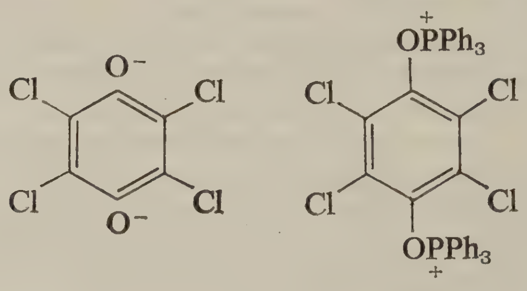
Benzoquinone and triphenylphosphine react to form the zwitter ion **V** which with hydrochloric acid or ethyl iodide may be converted to the normal phosphonium salt **VI**[182,186]:



**V** **VI**

(A = H, X = Cl; A = Et, X = I).

Chloranil reacts with difficulty to form the quasiphosphonium salt **VII**[2010]:



**VII**

## Properties of Phosphonium Compounds

Phosphonium salts, with the exception of hydroxides and alkoxides, are generally crystalline solids which dissolve in water without decomposition[1,2059] giving solutions having high electrical conductivity. They generally exhibit the properties of salts of strong bases with acids. The hydroxides and alkoxides are generally syrupy compounds which give strongly alkaline solutions.

Phosphonium compounds contain a 4-covalent tetrahedrally substituted phosphorus atom. Even so, it was not until 1947 that Mann and Holliman succeeded in resolving an asymmetric compound, the *P*-phenyl-*P*-*p*-hydroxyphenyl-*P*-*spiro*-1,2,3,4-tetrahydrophospholinium ion as its camphorsulphonate.[2060,2071] Since that time many asymmetric phosphonium salts have been resolved into their optical antipodes.[259,2042,2069] A useful review of the early attempts to resolve asymmetric phosphorus compounds is given by Mann.[2071] Reactions of optically active phosphorus compounds are reviewed by Hudson and Green,[574] and by Kamai and Usackeva.[2422] $^{31}P$ Chemical shifts in phosphonium salts are recorded.[2344]

### DECOMPOSITION OF PHOSPHONIUM HYDROXIDES

As a general rule, quaternary phosphonium hydroxides decompose when heated, either alone or in aqueous solution, to form a tertiary phosphine oxide and a hydrocarbon[141,269,271]:

$$R_1R_2R_3R_4P^+OH^- \rightarrow R_1R_2R_3PO + R_4H$$

Fenton and Ingold[269] studied the decomposition of phosphonium hydroxides of the type $R_3P^+R'OH^-$ ($R$=alkyl, phenyl; $R'$=arylalkyl, alkyl, phenyl) and from the observed order of preferential group elimination as hydrocarbon (benzyl > phenyl > methyl > 2-phenylethyl > ethyl > higher alkyl) concluded that the reaction involves the formation of an intermediate penta-covalent phosphonium hydroxide, $R_4P\text{–}OH$, which undergoes decomposition with elimination of the group having the greatest tolerance for a negative charge. This conclusion has been fully substantiated by more recent work on the decomposition of aryltriphenylphosphonium salts,[2039] alkyltriarylphosphonium salts[1956] and compounds of the type $\overset{\frown}{(\mathrm{CH_2})_n}\overset{+}{\mathrm{P}}(\mathrm{Ph})\mathrm{MeX}^-$ [2345] with strong aqueous alkali. The relative ease of elimination of aryl groups as aromatic hydrocarbons are: *o*-, *m*-, *p*-nitrophenyl > *p*-chlorophenyl > *p*-carbethoxyphenyl > *p*-diphenyl > α- and β-naphthyl > phenyl > *p*- and *m*-aminophenyl > *p*- and *m*-tolyl > *p*- and *m*-hydroxyphenyl.[2039]

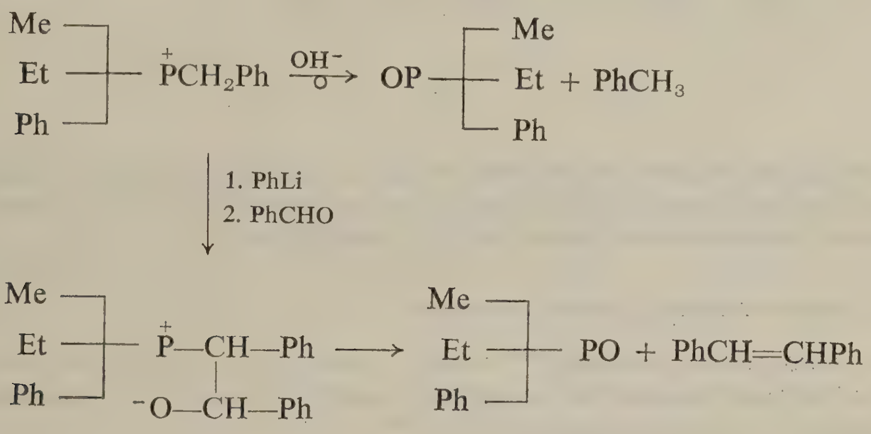
Kinetic studies of the decomposition of ethylmethylphenylbenzylphosphonium chloride[2044] and iodide[2040] and a number of *para*-substituted benzylphosphonium salts[2045] with aqueous alkali show that the reaction rates obey a third-order rate equation, $k \propto [R_4P^+][OH^-]^2$. It is generally accepted that the reaction proceeds by attack of hydroxide ion on a transient covalent adduct of the phosphonium cation and hydroxide ion[278, 2040, 2044]:

$$R_4P^+OH^- \overset{\text{fast}}{\rightleftharpoons} R_4P\text{—}OH \underset{\text{fast}}{\overset{OH^-}{\rightleftharpoons}} R_4P\text{—}O^- \xrightarrow{\text{slow}} R_3PO + R^-$$

and

$$R^- + H_2O \rightarrow RH + OH^-$$

The conversion of optically active ethylmethylphenylbenzylphosphonium chloride or iodide to ethylmethylphenylphosphine oxide with aqueous base is stereospecific and involves inversion of configuration at the phosphorus atom.[2041, 2043–4] The Wittig reaction of the phosphonium chloride with benzaldehyde to form stilbene and the same phosphine oxide is stereospecific and occurs with retention of configuration at phosphorus[2044]:



Further evidence which indicates inversion of configuration at the phosphorus atom in phosphonium salts on treatment with alkali has been advanced by Horner.[42, 44, 46]

The mechanism of the hydroxide cleavage of tetrakis(hydroxymethyl)phosphonium chloride to trishydroxymethylphosphine, formaldehyde and hydrogen has been examined.[279]

### *Exceptions to Normal Paraffinic Degradation*

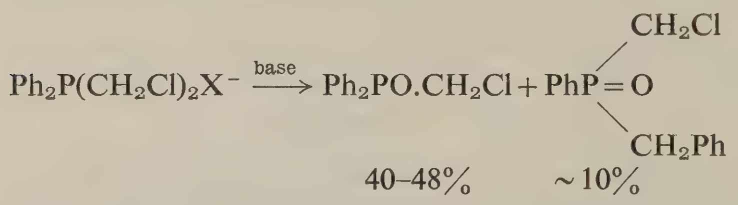
As indicated on page 896, phosphonium compounds having a 2-cyanoethyl substituent, a hydroxymethyl substituent, three or four chloromethyl substituents or a β,β-diphenylethyl substituent are decomposed by inorganic bases to form tertiary phosphine.

Tracer studies using tritium-labelled phosphonium salts of the type $R'CH_2CHR.P^+Ph_3X^-$ show that when R is a strongly electronegative substituent the compound first formed with hydroxide ion is not a pentavalent hydroxide adduct but the methylene phosphorane $R'CH_2CR{=}PPh_3$; this can form the phosphonium hydroxide and hence the tertiary phosphine oxide by addition of a water molecule:

$$R'CH_2C(R){=}PPh_3 \xrightarrow{H_2O} R'CH_2CHR.\overset{+}{P}Ph_3OH^- \rightarrow R'CH_2CH_2R + Ph_3PO$$

Compounds of the type $R_2P(CH_2Cl)_2Cl$ (R = ethyl, *cyclo*hexyl) and $Ph_3PCH_2Cl$[276, 2050] undergo normal paraffinic degradation with base to form methyl chloride and tertiary phosphine oxide, but diphenylbis(chloromethyl)phosphonium chloride gives a mixture of the expected product chloromethyldiphenylphosphine oxide and a product of rearrangement, benzylchloromethylphenylphosphine oxide.[276] Similar group migrations occur in bromomethyltriphenylphosphonium, methylmercaptomethyltriphenylphosphonium salts[2050] and phenyl tris(chloromethyl)phosphonium salts[2038]:

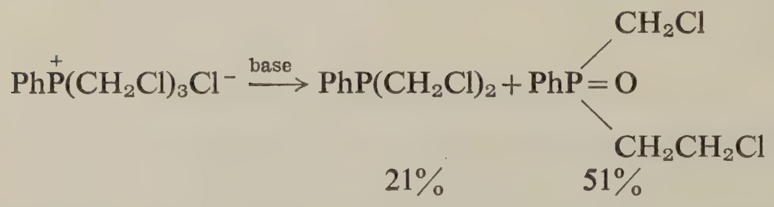
$$R_2\overset{+}{P}(CH_2Cl)_2X^- \xrightarrow{\text{base}} R_2PO.CH_2Cl + CH_3Cl \qquad (R = Et, Cy)$$



$$Ph_2P(CH_2Cl)_2X^- \xrightarrow{\text{base}} \underset{40\text{–}48\%}{Ph_2PO.CH_2Cl} + \underset{\sim 10\%}{PhP(CH_2Cl)(CH_2Ph){=}O}$$

$$Ph_3\overset{+}{P}CH_2YX^- \xrightarrow{\text{base}} Ph_3PO + Ph_2PO.CH_2Ph$$

$$17\%,\ Y = SMe$$
$$33\%,\ Y = Br$$



$$Ph\overset{+}{P}(CH_2Cl)_3Cl^- \xrightarrow{\text{base}} \underset{21\%}{PhP(CH_2Cl)_2} + \underset{51\%}{PhP(CH_2Cl)(CH_2CH_2Cl){=}O}$$

The ethynyl-substituted phosphonium compound $(C_6H_5)_2PC{\equiv}C\overset{+}{P}(C_6H_5)_2MeI^-$ is reported to undergo facile cleavage in warm water or ethanol giving diphenylmethylphosphine oxide and diphenylethynylphosphine.[94]

### DECOMPOSITION OF PHOSPHONIUM ALKOXIDES

There is no recent evidence[2016] which supports the claim that phosphonium alkoxides thermally decompose to tertiary phosphine oxide and hydrocarbon which was suggested by Hey and Ingold in 1933[268]:

$$R_4P^+OR' \xrightarrow{\Delta} R_3PO + R{-}R' \qquad (R = \text{methyl, benzyl, 2-phenylethyl})$$

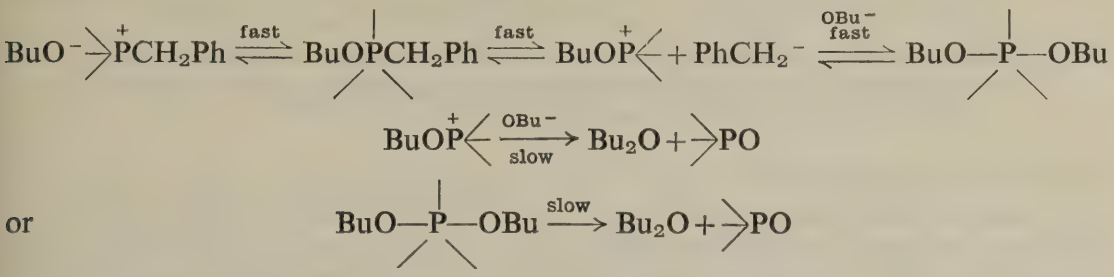
Grayson and Keough showed that benzyl-substituted phosphonium alkoxides are decomposed by heating in alcoholic solvent to tertiary phosphine oxide, a toluene and an ether[2046]:

$$R_3P^+CH_2ArX^- + NaOR \xrightarrow{ROH} R_3PO + ArCH_3 + R_2O + NaX$$

The same products are obtained by heating the corresponding methylenephosphorane with alcohol[2046]:

$$R_3P{=}CHAr + ROH \rightarrow R_3P^+CH_2ArOR^- \rightarrow R_3PO + ArCH_3 + R_2O$$

Under reflux in butanol solution optically active methylethylphenylbenzylphosphonium butoxide gives almost completely racemized methylethylphenylphosphine oxide (a slight net inversion of configuration occurs). The fact that, at room temperature, toluene is formed very much faster than dibutyl ether suggests the following reactions[2047]:



Tetra-alkyl- and phenyl-substituted phosphonium alkoxides behave differently from the benzyl compounds. Tetrabutylphosphonium butoxide shows no dissociation in butanol solution up to 200°C.[2046] With dry sodium ethoxide, tetrabutylphosphonium bromide decomposes at 240° to tributylphosphine and butene; no hexane is formed.[2016] Under similar conditions primary alkyltriphenylphosphonium salts decompose to *n*-alkyldiphenylphosphine and alkylphenyl ethers, but *iso*-propyltriphenylphosphonium iodide decomposes by the classical 'onium' route to triphenylphosphine and propene[2016, 2048]:

$$Ph_3\overset{+}{P}RX^- \xrightarrow{NaOR'} Ph_2PR + PhOR'$$

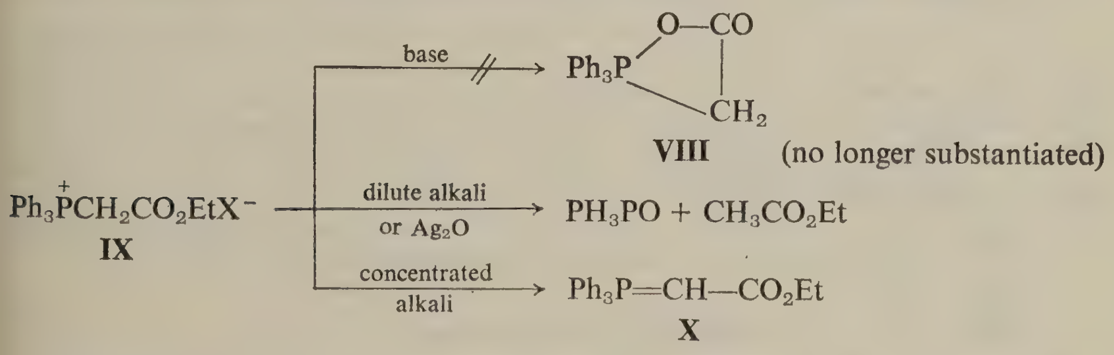
$$Ph_3P^+CHMe_3I^- \xrightarrow{NaOMe} Ph_3P + CH_3CH=CH_2$$

2-Hydroxyethyltriphenylphosphonium iodide is decomposed by alcoholic sodium alkoxide to 2-alkoxyethyldiphenylphosphine oxide and benzene; in aqueous solvents decomposition with hydroxide ion proceeds normally to give 2-hydroxyethyldiphenylphosphine oxide[2049]:

$$Ph_3\overset{+}{P}CH_2CH_2OH - \left| \begin{array}{l} \xrightarrow{RO^-/ROH} Ph_2PO.CH_2CH_2OR + PhH \\ \xrightarrow{OH^-/H_2O} Ph_2PO.CH_2CH_2OH + PhH \end{array} \right.$$

BETAINES

A number of early workers claimed the preparation of phosphonobetaines, **VIII**, by the action of alkali on phosphonoacetic ester, **IX**. More recent work shows that carbethoxymethyltriphenylphosphonium salts can react with alkali to form either a stable triphenylcarbethoxymethylene phosphorane **X** or the products of normal paraffinic degradation, depending on the concentration of the alkali used[2116–7]:



**VIII**

**IX**

**X**

Chloroacetic, $\beta$-chloropropionic and $\gamma$-chlorobutyric acids react with triphenylphosphine giving the corresponding carboxyalkyltriphenylphosphonium chlorides **XI.**[2118] The salt from chloroacetic acid undergoes decarboxylation on treatment with aqueous base; the other two salts form stable phosphonobetaines **XII**. There is no evidence that these phosphonobetaines have a pentacovalent structure.[2118] In contrast to chloroacetic acid, bromoacetic acid reacts like a typically positive halogen compound with triphenylphosphine to form the phosphine oxide and acetyl bromide.[2117-8] Triphenylphosphine and acrylic acid form triphenylphosphinopropionic betaine.[2346]

$$\underset{\textbf{XI}}{Ph_3\overset{+}{P}(CH_2)_nCO_2HCl^-} \xrightarrow[\text{aq}]{\text{NaOH}} \underset{\textbf{XII}}{Ph_3\overset{+}{P}(CH_2)_nCO_2^-} \qquad (n = 2, 3)$$

$$Ph_3P + BrCH_2CO_2H \xrightarrow[\text{no solvent}]{\text{benzene or}} Ph_3PO + CH_3COBr$$

MESOMERIC PHOSPHONIUM SALTS

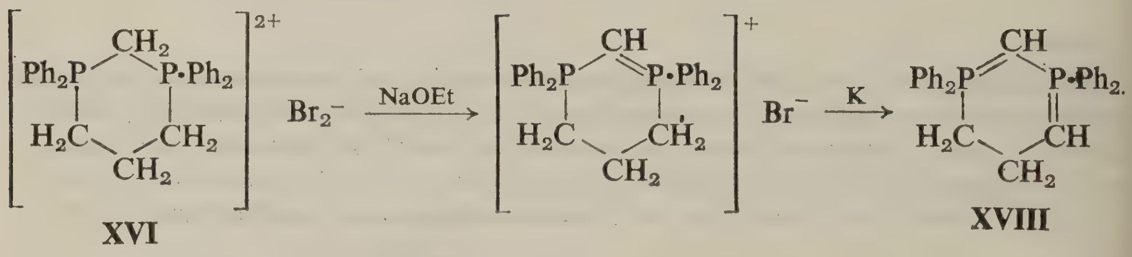
The reaction of triphenylphosphine and methylene dibromide to form methylenebistriphenylphosphonium dibromide[2028] led to the discovery of stable salts containing the stable triphenylphosphoniummethylenetriphenylphosphorane cation **XIII**.[2114] This cation is mesomeric as evidenced by a single $^{31}P$ n.m.r. absorption peak. Treatment with potassium gives the novel phosphorane hexaphenylcarbodiphosphorane **XIV** which reacts with hydrochloric acid to reform the mesomeric phosphonium salt and with bromine to form triphenylphosphoniumbromomethylenetriphenylphosphorane **XV**:

$$Ph_3\overset{+}{P}CH_2\overset{+}{P}Ph_3Br_2^- \xrightarrow{Na_2CO_3} \underset{\textbf{XIII}}{[Ph_3P\text{—}CH{=}PPh_3]^+Br^-} \xrightarrow[\text{diglyme}]{K} \underset{\textbf{XIV}}{Ph_3P{=}C{=}PPh_3}$$

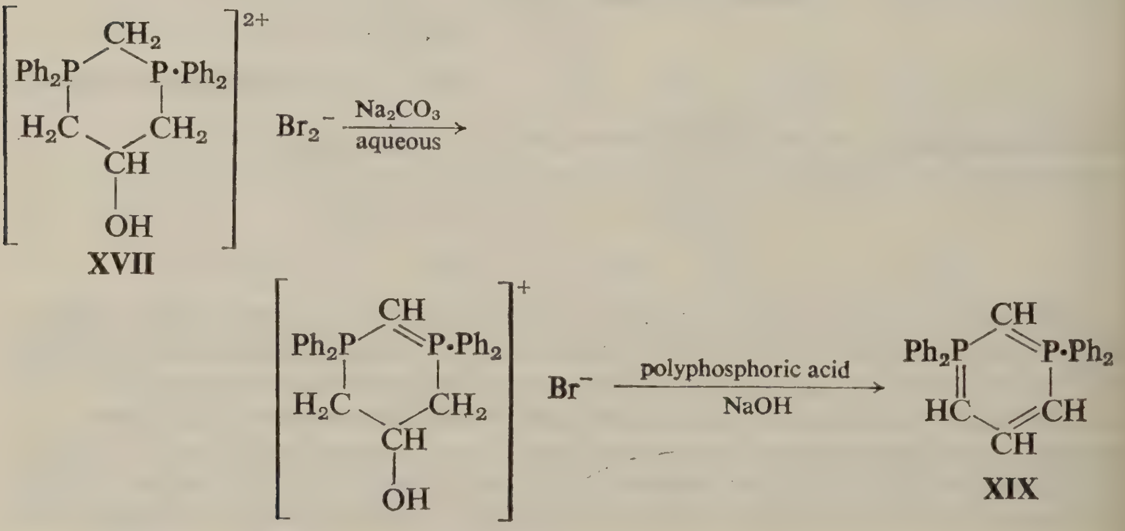
$$\downarrow Br_2$$

$$\underset{\textbf{XV}}{[Ph_3P\text{—}CBr{=}PPh_3]^+Br^-}$$

Similar mesomeric phosphonium compounds have been obtained from 1,1,3,3-tetraphenyl-1,3-diphosphonia*cyclo*hexane dibromide **XVI** and 1,1,3,3-tetraphenyl-1,3-diphosphonia-5-hydroxy*cyclo*hexane dibromide **XVII** which are themselves converted by base to yellow amorphous cyclic phosphoranes, 1,1,3,3-tetraphenyl-1,3-diphospha-4,5-dihydro*cyclo*hexane **XVIII** and 1,1,3,3-tetraphenyl-1,3-diphosphabenzene **XIX** respectively.[2115]



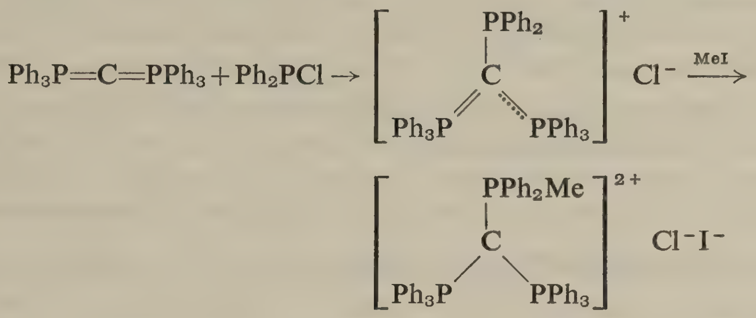
**XVI** **XVIII**



**XVII** **XIX**

1,1-Diphenyl-1-phosphabenzene,[2093] a yellow powder and 1,1-diphenylphosphanaphthalene[2095] have been obtained by similar routes by Märkl who has reviewed the chemistry of heterocyclic compounds of phosphorus.[2092] Heterocyclic phosphonium salts have been obtained by a number of workers.[218, 272, 2000, 2008]

A novel mesomeric phosphonium salt having three phosphorus atoms attached to one carbon atom is obtained from methylene bistriphenyl phosphorane[2347]:



### Applications of Phosphonium Compounds

The phosphonium salts have attained little commercial importance. The only compound which is at present produced in commercial quantities is tetrakishydroxymethylphosphonium chloride which is used in the flameproofing of cellulosic fibres. Compounds such as 3,4-dichlorobenzyltriphenylphosphonium chloride are substantive to wool and have been used as moth-proofing agents.[2091] Compounds of the type $R\overset{+}{P}Me_3X^-$ (where R is a long-chain alkyl group and X is a halogen), like the analogous nitrogen compounds, exhibit disinfectant properties.[2110] Tetrabutylphosphonium hydroxide has been used as a catalyst to bring about rearrangement and polymerization of siloxanes.[2125] Diquaternary phosphonium salts derived from tris(2,4,6-trimethoxyphenyl)phosphine are reported to show a high order of activity against influenza virus *in vitro*.[99] The antimyotic action of triphenyldecylphosphonium pentachlorophenoxide is more powerful than that of pentachlorophenol alone.[2128] Tetraphenylphosphonium chloride forms insoluble crystalline salts with the following anions: $BF_4^-$, $MnO_4^-$, $ReO_4^-$, $TeO_4^-$, $ClO_4^-$, $IO_4^-$ and the chloride complexes of a number of multiply charged metals; it has found some application in analytical chemistry.[2126] Benzyltriphenylphosphonium chloride has been used for the determination and extraction of rhenium.[2127]

## QUASIPHOSPHONIUM COMPOUNDS

Widely occurring in organophosphorus chemistry are four-covalent positively charged phosphorus compounds in which one or more of the atoms attached to phosphorus is oxygen, nitrogen, sulphur or halogen. Probably the only true phosphonium compounds in this class, i.e., those having an anion which is essentially ionic and metathetically replaceable in aqueous solution, are the *N*-quasi and *S*-quasi compounds. *O*-Quasiphosphonium salts and halogenophosphonium compounds are unstable to water, and are frequently formed as intermediates in the reactions of trivalent phosphorus compounds.[2075–6]

The first water-stable *O*-quasiphosphonium salt was isolated recently.[2351]

### *N*-Quasiphosphonium Compounds

PREPARATION

*From Phosphorous Amides*

Nitrogen analogues of the tertiary phosphines, i.e., phosphorous amides, $(R_2N)_3P$, phosphonous amides, $R'P(NR_2)_2$, and phosphinous amides, $R'_2PNR_2$, react readily with alkyl halides to form salt-like *N*-quasiphosphonium salts:

$$R'_2PNR_2 + R''X \rightarrow R'_2R''\overset{+}{P}NR_2X^- \qquad (R' = \text{alkyl, aryl, } NR_2)$$

Following the early work of Michaelis who demonstrated the quaternization of phosphorous tripiperidide,[2090] phosphorous tri-tetrahydroquinolide[446] and arylphosphonous dipiperidide[446] with alkyl and benzyl halides, a considerable number of *N*-quasiphosphonium compounds have been prepared by this route.[295,306,384,434,436,539,588,767,2094,2096]

The location of the methyl group on phosphorus in methylphenylbisdiethylaminophosphonium iodide, prepared from phenylphosphonous bisdiethylamide and methyl iodide, has been established by nuclear magnetic resonance.[384] Bis-(diphenylphosphino)methylamine, $(Ph_2P)_2NMe$, and methyl iodide form a monomethiodide shown by infra-red spectroscopy to be the phosphonium salt $Ph_2P.NMe.\overset{+}{P}Ph_2MeI^-$.[588] Halogens react with trisdimethylaminophosphine in inert solvents to form trisdimethylaminohalogenophosphonium halides. The salt-like character of these compounds has been demonstrated by conductimetric measurements in nitrobenzene, by the infra-red spectrum of the cation $(Me_2N)_3\overset{+}{P}Cl$ and by the preparation of complex salts such as $(Me_2N)_3\overset{+}{P}ClY^-$ (where $Y^- = NO_3^-, FeCl_4^-, BPh_4^-$).[2096] Solid compounds with well-defined melting points which may be regarded as *N,N,N,S*-quasiphosphonium halides are formed from hexa-*N*-alkylphosphorous triamides and alkyl/arylsulphenyl chlorides[2120] or by alkylation of phosphorotriamidothionates with *n*-alkyl iodides[2122]:

$$(R_2N)_3P + R'SCl \rightarrow (R_2N)_3P—SR'Cl$$
$$(RNH)_3PS + R'I \rightarrow (RNH)_3P—SR'I$$

Phenyl dimethylaminotrifluorophosphorane is reported to undergo rearrangement to phenylbis(dimethylamino)fluorophosphonium phenylpentafluorophosphate when allowed to stand at room temperature for several weeks. The anion represents one of the few hexa-coordinated species of phosphorus which have been reported.[1999]

### *From Halogenophosphoranes and Phosphorus Pentachloride*

*N*-Aryl substituted quasiphosphonium chlorides are formed by heating phosphorus pentachloride[2097-8] or aryl tetrachlorophosphoranes[2099] with primary aromatic amines:

$$PhPCl_4 + PhNH_2(\text{excess}) \rightarrow Ph\overset{+}{P}(NHPh)_3Cl^-$$

Alkylamino and dialkylaminotriphenylphosphonium salts are readily obtained from triphenyldihalogenophosphoranes and primary or secondary amines[2100-1]:

$$Ph_3PX_2 + RNH_2 \xrightarrow{Et_3N} Ph_3\overset{+}{P}NHRX^-$$

With phenylhydrazine the product is a triphenylphenylhydrazinophosphonium halide.

### *From Iminophosphoranes (Phosphine Imines)*

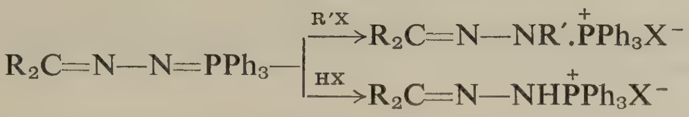
Iminophosphoranes may be regarded as the conjugate bases of *N*-quasiphosphonium salts, the relationship being formally similar to that between normal phosphonium salts and the methylenephosphoranes:

$$R_3P = NR' \underset{-HX}{\overset{+HX}{\rightleftharpoons}} R_3\overset{+}{P}—NHR'X^-$$

They have basic character,[110,2108] readily add hydrogen halides and react with alkyl halides to form the *N*-quasiphosphonium salts.[11,2100] Alkylaminotriphenylphosphonium salts have been converted to dialkylaminotriphenylphosphonium salts *via* the iminophosphorane:

$$Ph_3\overset{+}{P}NHRBr^- \xrightarrow[NH_3]{NaNH_2} Ph_3P{=}NR \xrightarrow{MeI} Ph_3\overset{+}{P}NRMeI^-$$

Phosphazines,[177] e.g., formaldehyde triphenylphosphazine $CH_2{=}N{-}N{=}PPh_3$, are alkylated by alkyl halides to form $N^{\beta}$-alkylidene-$N^{\alpha}$-alkylhydrazinotriphenylphosphonium salts; hydrogen halides give the $N^{\beta}$-alkylidenehydrazinophosphonium salts[2102]:



$$R_2C{=}N{-}N{=}PPh_3 \xrightarrow{R'X} R_2C{=}N{-}NR'.\overset{+}{P}Ph_3X^-$$
$$R_2C{=}N{-}N{=}PPh_3 \xrightarrow{HX} R_2C{=}N{-}NH\overset{+}{P}Ph_3X^-$$

In contrast the reaction of $\alpha$-ketophosphazines, $RCOCH{=}N{-}N{=}PPh_3$, with methyl iodide involves P–N bond fission to form a diazoketone and a normal phosphonium salt.[2103]

*From Tertiary Phosphines*

Tertiary phosphines react with solutions of chloramine forming aminophosphonium salts:

$$R_3P + ClNH_2 \rightarrow R_3\overset{+}{P}NH_2Cl^- \qquad (R = \text{alkyl, aryl, benzyl, 2-cyanoethyl})$$

The reactions proceed almost quantitatively based on the quantity of chloramine or phosphine consumed. Stable aminophosphonium salts such as the chloroplatinate, picrate, periodate and nitroprusside may be obtained from the chloride by double decomposition reactions.[2104-5, 2162] *N*-Substituted aminophosphonium salts are obtained using chloramines such as *N*-methylchloramine,[2104] *N*-benzylchloramine[2121] and *N*-chlorourea.[2161] Aminophosphines $(R_2N)_3P$, $(R_2N)_2PR'$, $R_2NPR'_2$, $RN(PPh_2)_2$ (where R = methyl, ethyl, R′ = methyl, butyl, phenyl) and hydrazinophosphines $RP(NHNMe_2)_2$ (where R = methyl, phenyl) react like tertiary phosphines with chloramine to form the corresponding aminosubstituted phosphonium salts.[2162, 2348, 2350] Triphenylaminophosphonium hydrogen sulphate can be prepared from triphenylphosphine and hydroxylamine-*O*-sulphonic acid.[2107]

The reaction of triphenylphosphine and hydrazoic acid was investigated by Staudinger and Hauser[110] who formulated the product as $Ph_3P{=}NH.N_3H$; recent work indicates the product to be triphenylaminophosphonium azide.[2106, 2109]

Salts of mesomerically stabilized bistriphenylphosphine nitride cation have been obtained by reaction of triphenylphosphine imine (iminotriphenylphosphorane) with dibromotriphenylphosphorane[2108] and by pyrolysis of triphenylaminophosphonium azide[2109]:

$$Ph_3P{=}NH + Ph_3PBr_2 \rightarrow [Ph_3P{=}N{-}P.Ph_3]^+Br^- + Ph_3\overset{+}{P}NH_2Br^-$$
$$Ph_3\overset{+}{P}NH_2N_3^- \rightarrow [Ph_3P{=}N{-}P.Ph_3]^+N_3^-$$

### GENERAL PROPERTIES OF *N*-QUASIPHOSPHONIUM COMPOUNDS

These compounds are frequently crystalline solids and are soluble in water without decomposition. Like the phosphonium salts, they undergo decomposition in hot alkaline solution to form an amine and a phosphoryl compound.[110, 903, 943, 2101]

$$R_3\overset{+}{P}NR'_2X^- \xrightarrow{H_2O/NaOH} R_3PO + R'_2NH$$
$$(R = \text{alkyl, aryl, } NR'_2;\ R' = \text{H, alkyl, aryl})$$

Hydroxides of tetra-(*N*-arylamino)phosphonium salts are reported to be syrupy neutral substances.[2099]

*N*-Quasiphosphonium compounds derived from hexa-*N*-substituted phosphorous triamide[295, 434] or tetra-*N*-substituted phenylphosphonous diamide[436] and methyl or benzyl halides undergo the Wittig reaction:

$$(R_2N)_2R'\overset{+}{P}CH_2Ph \xrightarrow[PhCHO]{NaOMe} (R_2N)_2R'PO + PhCH{=}CHPh \qquad (R' = \text{Ph or } R_2N)$$

*N*-Phenylaminotriphenylphosphonium chloride is readily decomposed by electrolysis to triphenylphosphine and aniline[2013]:

$$\mathrm{Ph_3\overset{+}{P}NHPhCl^- \rightarrow Ph_3P + PhNH_2 + HX}$$

Compounds such as di-(*tert*-butylamino)methylphenylphosphonium iodide are claimed to be fungicides.[306]

## *O*-Quasiphosphonium Compounds

Aryl esters of phosphorous,[813, 903, 916] phosphonous[421] and phosphinous[421, 920] acids react readily with alkyl halides such as methyl iodide or benzyl chloride to form *O*-quasiphosphonium compounds of the type $\mathrm{(ArO)_3\overset{+}{P}RX^-}$, $\mathrm{(ArO)_2\overset{+}{P}RR'X^-}$ and $\mathrm{ArO\overset{+}{P}RR'_2X^-}$ respectively. These compounds are readily hydrolyzed by water or dilute alkali to give a phosphoryl compound and a phenol.[421, 813, 916, 943] They react with alcohols to form the corresponding alkyl halide.[813, 2111] Thermal decomposition of the *O*-phenyl compounds at about 300° gives iodobenzene.[421] Reduction of methyltriphenoxyphosphonium iodide gives disodiummethylphosphine[36]:

$$\begin{array}{r}\mathrm{(PhO)_2PO.Me + PhI} \xleftarrow{\Delta} \\ \mathrm{MePNa_2} \xleftarrow{\mathrm{Na}}\end{array}\left|\mathrm{—(PhO)_3PMeI—}\right|\begin{array}{l}\xrightarrow{\mathrm{H_2O}} \mathrm{(PhO)_2PO.Me + PhOH + HI} \\ \xrightarrow{\mathrm{ROH}} \mathrm{(PhO)_2PO.Me + PhOH + RI}\end{array}$$

The reaction of triphenoxymethylphosphonium iodide with silver nitrate in alcoholic solution is reported to be slow.[813] With silver acetate or silver nitrate in acetonitrile solution there is an immediate precipitate of silver iodide, the reaction products being diphenyl methylphosphonate together with phenyl acetate or a mixture of *o*- and *p*-nitrophenols respectively. Under similar conditions but with silver nitrate and an alcohol an alkylphenylmethylphosphonate results[2112-3]:

$$\mathrm{MeP(OPh)_3I \xrightarrow[(AgNO_3)]{AgOAc} (PhO)_2PO.Me + AgI + PhOAc(HOC_6H_4NO_2)}$$

2,2,2-Triphenylethanol and tributyldibromophosphorane form 2,2,2-triphenylethoxytributylphosphonium bromide which, in contrast to other alkoxyphosphonium compounds,[920] is stable to water.[2351]

*O*-Quasiphosphonium fluoroborates having alkoxy and aryloxy substituents have been obtained by reaction of tertiary phosphites with oxonium and carbonium ion fluoroborates such as triethyloxonium fluoroborate and triphenylcarbonium fluoroborate. Ethyltriethyloxyphosphonium fluoroborate is readily decomposed by alcoholic alkoxide solution to form diethyl ethylphosphonate and an ether[921-2]:

$$\mathrm{(EtO)_3P + Et_3O^+BF_4^- \rightarrow (EtO)_3\overset{+}{P}EtBF_4^- + Et_2O}$$
$$\mathrm{(EtO)_3\overset{+}{P}EtBF_4^- \xrightarrow[PrO^-]{PrOH} EtPO(OEt)_2 + PrOEt}$$

*N*-Quasiphosphonium fluoroborates are obtained similarly using trisdialkylaminophosphines or by displacement of triphenyl phosphite from triphenylmethyltriphenoxyphosphonium fluoroborate.[921-2]

$$\mathrm{Ph_3C\overset{+}{P}(OPh)_3BF_4^- + (Me_2N)_3P \rightarrow Ph_3C\overset{+}{P}(NMe_2)_4BF_4^- + (PhO)_3P}$$

*O*-Aryl and *S*-aryl triphenylphosphonium bromides are obtained from triphenyldibromophosphorane and a phenol or mercaptan[1987]:

$$\mathrm{Ph_3PBr_2 + ArXH \xrightarrow{Et_3N} Ph_3\overset{+}{P}XArBr^-} \qquad (\mathrm{X = O, S})$$

### *S*-Quasiphosphonium Salts

Trialkylthioalkylphosphonium iodides result from the alkylation of trialkylphosphine sulphides with alkyl iodides.[176] They behave as normal dissociated salts in aqueous solution. Hydrolysis takes place slowly in hot water giving mercaptan and trialkylphosphine oxide; in alkaline solution hydrolysis is rapid giving the phosphine oxide with a predominant inversion of configuration[46]:

$$Et_3PS + MeI \rightarrow Et_3\overset{+}{P}SMeI^- \xrightarrow{H_2O} Et_3PO + MeSH + HI$$

## METHYLENEPHOSPHORANES

Methylenephosphoranes, **II**, are formed by the elimination of hydrogen halide from phosphonium compounds, **I**, having an $\alpha$-hydrogen atom. They add hydrogen halide, reforming the phosphonium salt. Bestmann considers that phosphonium salts can be regarded as Brønsted acids, and the alkylidenephosphoranes as their conjugate bases.[2011, 2129] The methylenephosphoranes themselves are best represented as resonance hybrids of contributing structures such as **II** and **III**:

$$\begin{array}{ccccc} R_3\overset{+}{P}CHR_1R_2X^- & \underset{+HX}{\overset{-HX}{\rightleftharpoons}} & R_3P{=}CR_1R_2 & \leftrightarrow & R_3\overset{+}{P}\overset{-}{C}HR_1R_2 \\ \textbf{I} & & \textbf{II} & & \textbf{III} \end{array}$$

The stability and reactivity of methylenephosphoranes vary widely, depending on the substituents attached to the phosphorus atom and to the $\alpha$-carbon atom. Generally the compounds may be isolated as red or yellow crystalline solids. The alkylidenetriphenylphosphoranes are highly reactive; they react with oxygen, hydrogen halides, water, alcohols and carbonyl compounds. Arylidenetriphenylphosphoranes are somewhat less reactive and the diarylidene compounds are stable to oxygen and carbonyl compounds but react with water and alcohols. In extreme cases the compounds may be prepared in aqueous solution and show remarkable stability.

Electron-attracting groups attached to the $\alpha$-carbon atom increase the acidity of the phosphonium salt and decrease the reactivity of the corresponding phosphorane. Thus, alkylidenetriphenylphosphoranes are difficult to isolate and can be prepared only by the action of bases such as phenyl lithium and butyl lithium in inert media on the appropriate phosphonium salts. On the other hand dilute aqueous base is sufficient to convert triphenyl-9-fluorenylphosphonium bromide,[2133] triphenyl-*cyclo*pentadienyl bromide,[2134] triphenyl-*p*-nitrobenzylphosphonium bromide[2135] and compounds of the type $Ph_3\overset{+}{P}CH_2YX^-$ ($Y = CN, COR, CO_2R$)[2116, 2131] to the corresponding phosphoranes.

Electron-attracting groups attached to phosphorus facilitate formation of the phosphorane from the phosphonium salt but increase the reactivity of the phosphorane to reagents such as water. Thus, in compounds $R_3PCH_2CO_2CH_3$, when $R = Ph$, deprotonation can be effected by dilute sodium carbonate solution[2129] but when R = *cyclo*hexyl, dilute sodium hydroxide is required.[2130] The *cyclo*hexyl compound is decomposed by cold water whereas the phenyl compound decomposes only on boiling.

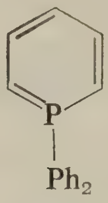
Transylidation reactions, e.g.,

$$Ph_3P{=}CH_2 + Ph_3\overset{+}{P}CH_2COR \rightleftharpoons Ph_3\overset{+}{P}CH_3 + Ph_3P{=}CHCOR$$

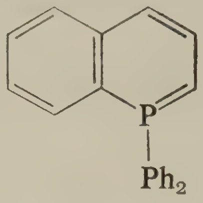
afford a useful method of comparing the strength of mesomeric and inductive effects of substituents on the acidity of the hydrogen atoms of the methylene group adjacent to phosphorus and on the basicity of the phosphorane. The acidity of the hydrogen atoms decreases in the series, substituent $= C_6H_5CO > CH_3CO_2 > C_6H_5 >$ alkyl.[2129]

Particularly interesting examples of stable phosphoranes are compounds such as

IV and V. These possess definite aromatic character, do not react with carbonyl compounds and are relatively stable to hydrolysis[2093, 2095]:



**IV**



**V**

## Preparation of Alkylidenephosphoranes

The first alkylidenephosphorane, diphenylmethylenetriphenylphosphorane, was made by Staudinger and Meyer[177] in 1919 by the thermal decomposition of the phosphazine obtained from triphenylphosphine and diphenylketen:

$$Ph_3P + Ph_2CN_2 \rightarrow Ph_3P{-}N{=}N{=}CPh_2 \xrightarrow{\Delta} Ph_3P{=}CPh_2 + N_2$$

In 1924 Isler[2136] obtained the same compound by treating the corresponding phosphonium compound with potassium:

$$Ph_3\overset{+}{P}CHPh_2Br^- \xrightarrow[-KBr]{K} Ph_3P{=}CPh_2$$

Of particular interest is the early work which showed that the above phosphorane would react with phenylisocyanate[177] or with diphenylketene[2137] giving diphenylketene isocyanate and tetraphenylallene respectively, together with triphenylphosphine oxide.

The potentialities of these reactions lay dormant for some 30 years until 1953 when Wittig and co-workers[5, 125, 2140] showed that triphenylalkylidenephosphoranes, formed by the action of bases such as phenyl lithium on $Ph_3\overset{+}{P}CH_2RX^-$, would react with aldehydes and ketones to form an intermediate betaine which decomposed to triphenylphosphine oxide and an olefin:

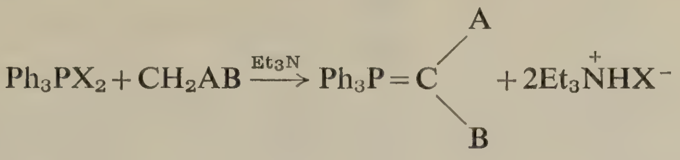
$$Ph_3P{=}CR_1R_2 + R_3R_4CO \rightarrow [\text{complex}] \rightarrow Ph_3PO + R_1R_2C{=}CR_3R_4$$

Wittig's work provided the stimulus to a considerable number of investigations and over the last 10 years there is little doubt that more papers have been published on the Wittig and related reactions than on any other branch of organophosphorus chemistry. A number of reviews of this work are available.[1998, 2004, 2011–3, 2138, 2143–6, 2158]

The most important method of preparation is by the action of suitable bases on alkylphosphonium salts:

$$R_3\overset{+}{P}CH_2R'X^- \xrightarrow[-BH]{B} R_3P{=}CHR'$$

As indicated earlier the strength of the base required depends on the acidity of the $\alpha$-hydrogen atom and can vary from aqueous sodium carbonate for compounds such as $(Ph_3\overset{+}{P})_2CH_2\,Br_2^-$ [2128] to alkali metals in non-polar solvents for compounds such as $Ph_3\overset{+}{P}CH_3Br^-$. Methods of lesser importance are the reaction of carbenes with triphenylphosphine to form halogenomethylenetriphenylphosphoranes,[2021] the formation of triphenylmethylenephosphorane by the reaction of diphenylmethylphosphine with benzyne[2148] or with diazomethane in the presence of copper,[2035] the reaction of triphenylphosphine with carbon tetrahalides to give compounds of the type $Ph_3P{=}CX_2$,[2024–5] and the formation of stable phosphoranes of the type $Ph_3P{=}CAB$ (A, B = CN, $CO_2R$, COR, $PhSO_2$, etc.) from triphenyldihalogenophosphoranes and active methylene compounds[582, 1000]:



$$Ph_3PX_2 + CH_2AB \xrightarrow{Et_3N} Ph_3P{=}C\begin{matrix}A\\ \\B\end{matrix} + 2Et_3\overset{+}{N}HX^-$$

### Reactions of Methylenephosphoranes

The importance of alkylidenephosphoranes stems from their use as intermediates for the preparation of a wide variety of organic compounds which may be obtained in high yield and purity by single-stage condensation reactions. Many of these compounds can be prepared in but poor yield by multi-stage classical organic chemical methods. Outstanding examples of the use of alkylidenephosphoranes as synthetic intermediates are in the following fields: naturally occurring polyenes and polyenic acids, Vitamin D, Vitamin A and carotenoids, *cyclo*propanes and acetylene derivatives. General reactions of phosphine methylenes are set out in Chart VII and on pages 927–931.

## ACID DERIVATIVES HAVING ONE OR TWO P–C BONDS

### Phosphonous Dihalides ($RPX_2$), Phosphinous Halides ($R_2PX$)

These compounds form an important class of intermediates for the preparation of acids and acid derivatives which contain one or two phosphorus–carbon bonds. The majority of the compounds recorded are chlorides. A few bromides and iodides are known and have usually been obtained from the corresponding chlorides by halide exchange reactions.

Relatively few phosphonous and phosphinous fluorides are reported. Halogenophosphines, in general, undergo both oxidation and fluorination with reagents such as antimony trifluoride or arsenic trifluoride, to form derivatives of phosphorus pentafluoride[302, 340, 556, 891, 991] (cf. page 958). Exceptions are halogenophosphines having negative substituents such as chloromethylphosphonous dichloride,[556, 2361–2] trifluoromethylphosphonous di-iodide,[302] bis(trifluoromethyl)phosphinous iodide, trifluorovinylphosphonous dichloride and bis(trifluorovinyl)phosphinous chloride[2432] which yield the corresponding fluorophosphines. Compounds such as phenylphosphonous dichloride may be converted to the corresponding fluorophosphines using sodium fluoride in tetramethylene sulphone solvent.[2431] Methyl phosphonous difluoride, formed from the chloro compound and potassium fluoride, decomposes slowly at room temperature to a mixture of methyl tetrafluorophosphorane and pentamethyl*cyclo*pentaphosphine. It reacts with nickel carbonyl giving a relatively stable complex $Ni(CH_3PF_2)_4$.[2360]

The more important general methods for preparing phosphonous and phosphinous halides are outlined below.

### Friedel–Crafts Synthesis

This method has been used extensively to prepare organophosphorus compounds and is one of the best for those in which phosphorus is linked to an aromatic nucleus[303]:

$$ArH + PCl_3 + AlCl_3 \rightarrow ArPCl_2{,}AlCl_3 + HCl$$

The complex of aluminium chloride and arylphosphonous dichloride may be broken by treatment with phosphorus oxychloride,[303] pyridine,[304] or water.[305] Treatment of

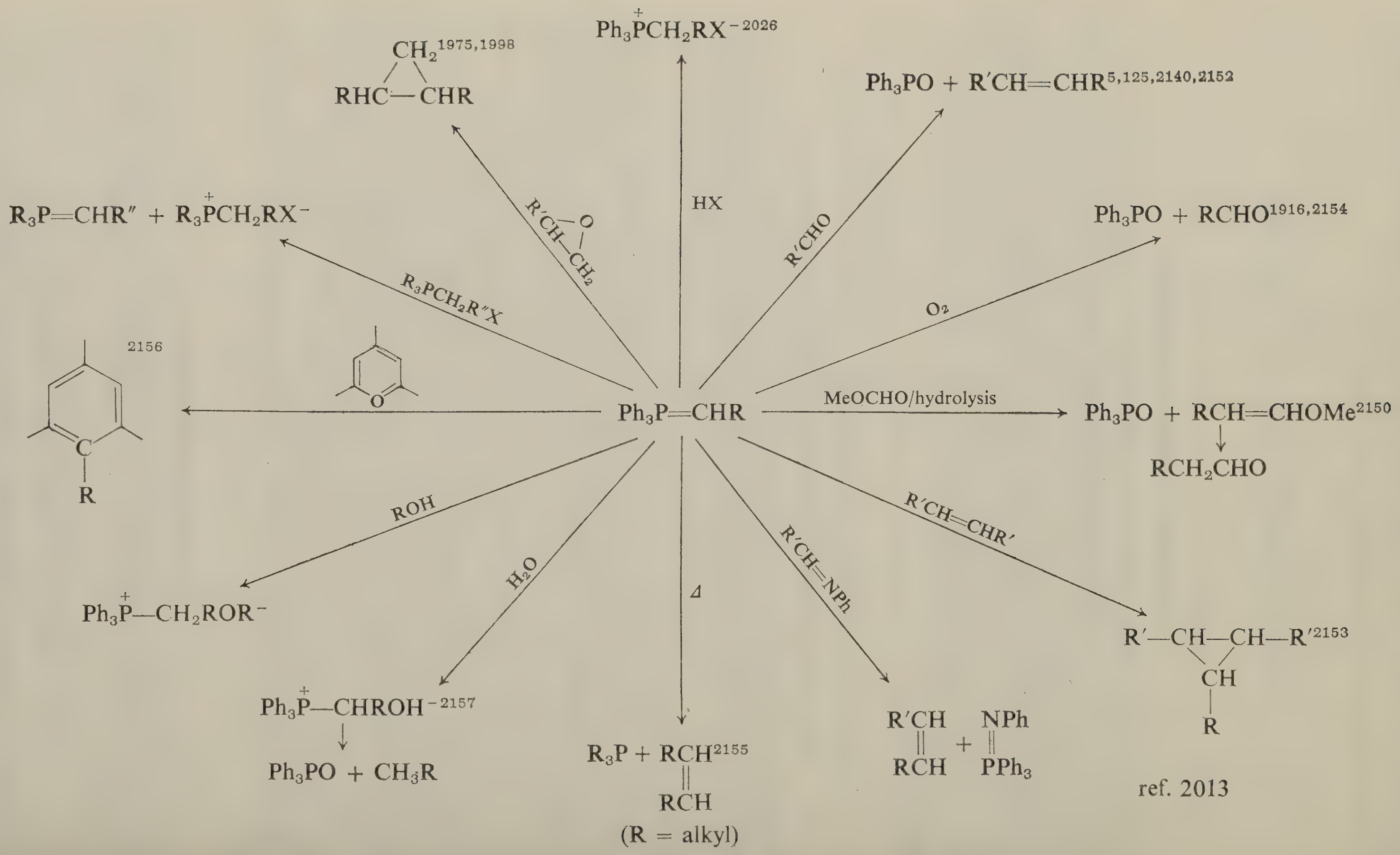


CHART VII.—General reactions of methylene phosphoranes the complex with an alcohol or phenol,[308] or with chlorine followed by an alcohol or phenol[309] gives the phosphonous and phosphonic ester respectively:

$$ArPCl_2,AlCl_3-\left|\begin{array}{l}\xrightarrow{POCl_3} ArPCl_2+POCl_3,AlCl_3\\ \xrightarrow{C_5H_5N} ArPCl_2+C_5H_5N,AlCl_3\end{array}\right.$$

A disadvantage of the Friedel–Crafts method is the formation of isomers; toluene gives *ortho*:*meta*:*para* isomers in the ratios 10:27:63.[307] Recent work throws doubt on the formation of the *ortho* compound. Toluene was found to yield two isomeric dichlorophosphines, *para* and *meta* in a ratio close to 2:1[547]; ethylbenzene[579] gave ethylphenyldichlorophosphines in a *para*:*meta* ratio of 1·63:1.

Isomer ratios of the products, $X–C_6H_4–PCl_2$, from $C_6H_5X$ and phosphorus trichloride (X = halogen, alkyl) have been investigated by Schindlbauer. Fluorobenzene gives the following isomer-percentage products: *ortho*- 5%, *meta*- 2%, *para*- 93%. The other halogenobenzenes give mainly *p*-isomer with little *ortho*- or *meta*-isomers; alkylbenzene gives little *ortho*-isomers, but *meta*-isomers in up to 40% yield.[2354] The Friedel–Crafts reaction of *o*-chlorotoluene and phosphorus trichloride followed by conversion of the products to phosphonic acids gives equal amounts of 3-chloro-4-tolylphosphonic acid and 4-chloro-3-tolylphosphonic acid.[2355]

Tertiary aromatic amines, such as dimethylaniline react with phosphorus trichloride (without catalyst or in the presence of aluminium chloride) giving, by successive replacement of the chlorine atoms, *p*-dialkylaminophenylphosphonous dichloride,[424, 1742–4] bis(*p*-dialkylaminophenyl)phosphinyl chloride,[424–5] and tris(*p*-dialkylaminophenyl)phosphine.[230, 424–5] Aqueous treatment of the chloro compounds gave the phosphonous acid and diarylphosphine oxide.[424] Anisole and phosphorus trichloride react under reflux with ferric chloride as catalyst to form isomeric methoxyphenylphosphonous dichlorides.[197]

### REACTION OF PHOSPHORUS TRICHLORIDE WITH ORGANOMETALLIC COMPOUNDS

Grignard reagents and organolithium compounds generally react with phosphorus trichloride giving exclusively tertiary phosphines.[310] By reverse addition, phosphinous chlorides have been obtained in good yield[528] from Grignard reagents. Organometallic compounds of mercury,[311] cadmium,[312, 2356] zinc,[310] aluminium,[313–4] and lead[315, 232] react with the trichloride giving phosphonous dichlorides:

$$\begin{array}{l}R_2Hg+PCl_3\rightarrow RPCl_2+RHgCl\\ RZnBr+PCl_3\rightarrow RPCl_2+ZnBrCl\\ R_3Al+3PCl_3\rightarrow 3RPCl_2+AlCl_3\\ Et_4Pb+3PCl_3\rightarrow 3EtPCl_2+PbCl_2+EtCl\end{array}$$

Phosphinous halides are often formed as by-products and under more vigorous conditions it is possible to prepare phosphinous chlorides from phosphorus trichloride or phosphonous chlorides using organic compounds of lead,[232, 316] zinc,[317] and mercury[318]:

$$R'PCl_2+HgR_2\rightarrow RR'PCl+RHgCl$$

Tetraethyl tin is reported to react with phosphorus tribromide but not with phosphorus trichloride.[319] Phosphorus trichloride will abstract a phenyl group from triphenyl bismuth and triphenyl stibine but not from triphenyl arsine.[529]

### REDUCTION OF COMPLEXES OF TYPE $R\overset{+}{P}Cl_3.A^-$ AND $R_2PX_2^+.A^-$

Alkyl phosphonous dichlorides are much more difficult to prepare than the aryl compounds. Recently it has been shown possible to reduce Kinnear–Perren complexes (see p. 954) with aluminium, phosphorus or sodium[321] or metal hydride[2357] in the presence of an alkali metal halide, with aluminium in methyl cyanide,[399] or with antimony powder in dibutyl phthalate[297, 332] to yield the phosphonous dichloride. Alkylarylphosphinous halides have been similarly prepared from the complex formed from aryldichlorophosphines[530]:

$$RCl + AlCl_3 + PCl_3 \rightarrow RPCl_3{,}AlCl_4 \xrightarrow{Al} RPCl_2{,}AlCl_3 + AlCl_3 \xrightarrow{KCl} RPCl_2 + 2KAlCl_4$$

$$RCl + AlCl_3 + ArPCl_2 \rightarrow RArPCl_2{,}AlCl_4 \xrightarrow{Al,\ KCl} R(Ar)PCl + KAlCl_4$$

Aryl dichlorophosphines are prepared by reducing aryl trichlorophosphonium fluoroborates (see p. 968) with magnesium,[531] or better, aluminium[532]:

$$Ar\overset{+}{P}Cl_3.BF_4^- \xrightarrow{Al} ArPCl_2$$

Diarylphosphinous chlorides are obtained by preparing the fluoroborate from an arylphosphonous dichloride rather than from phosphorus trichloride.[337, 532]

### REACTIONS OF ALKYL HALIDES WITH ELEMENTAL PHOSPHORUS

Elemental, especially white (P(w)), phosphorus and alkyl[205, 322] or aryl[322] halides and perfluoroalkyl iodides[154, 240] react at elevated temperature giving mixtures of organophosphorus compounds:

$$\begin{aligned}&CF_3I + P(w) \rightarrow CF_3PI_2 + (CF_3)_2PI + (CF_3)_3P\\&PhBr + P(w) \xrightarrow{300^\circ} PhBr_2 + Ph_2PBr \text{ [322, 2057]}\\&C_8H_{17}Br + P(w) \xrightarrow{250\text{–}270^\circ} C_8H_{17}PBr_2 + (C_8H_{17})_2PBr \text{ [322]}\end{aligned}$$

The phosphonous dihalides can be made to predominate.

Red phosphorus and alkyl or aryl halides react in the presence of copper powder giving mixtures of products in which the phosphonous dihalide predominates[323, 533, 2358]:

$$MeCl + P \xrightarrow{Cu} MePCl_2 + Me_2PCl$$

Carbon tetrachloride and white phosphorus react to form trichloromethylphosphonous dichloride, $CCl_3PCl_2$.[335]

### MISCELLANEOUS METHODS

Many methods have been described which give good yields of specific compounds. Phenylphosphonous dichloride is prepared[324-5] when a mixture of benzene and phosphorus trichloride is pyrolyzed at about 700°. Diphenylphosphinous chloride may be prepared by disproportionating the dichloride by pyrolysis[327] or by distillation with aluminium trichloride[326]:

$$\begin{aligned}PCl_3 + C_6H_6 &\rightarrow C_6H_5PCl_2 + HCl\\2C_6H_5PCl_2 &\rightarrow (C_6H_5)_2PCl + PCl_3\end{aligned}$$

An alternative route to this compound is from benzene and phosphorus pentasulphide *via* diphenylphosphinodithioic acid[328-9]:

$$P_2S_5 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_2PS_2H \xrightarrow{Cl_2} (C_6H_5)_2PCl_3 \xrightarrow{P} (C_6H_5)PCl$$

Dimethylphosphinous chloride can be obtained from tetramethyldiphosphine disulphide by reaction with phenyldichlorophosphine[1316]:

$$(Me_2PS)_2 + PhPCl_2 \rightarrow 2Me_2PCl + PhPS$$

The adducts formed by the addition of phosphorus pentachloride to olefines are reduced by elemental phosphorus giving $\alpha$-$\beta$-unsaturated phosphonous dichlorides.[331] Thermal decomposition of dihalogenophosphoranes has found limited application for the preparation of alkylarylphosphinous chlorides.[1] Reduction of tetrachlorophosphoranes with methyl phosphorodichloridite is reported[1504]:

$$CH_3PCl_4 + CH_3OPCl_2 \rightarrow CH_3PCl_2 + POCl_3 + CH_3Cl$$

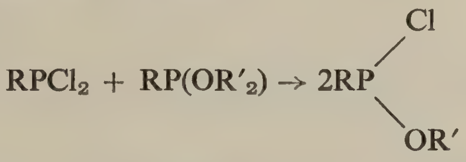
Halogenation, under carefully controlled conditions, of primary and secondary phosphines and phosphine derivatives which contain a P–P bond gives moderate yields of phosphonous and phosphinous halides. A method of potentially wide application involves chlorinating phosphines with phosgene[143, 333, 534]:

$$RPH_2 + 2COCl_2 \rightarrow RPCl_2 + 2CO + 2HCl$$
$$R_2PH + COCl_2 \rightarrow R_2PCl + CO + HCl$$

Grignard reagents and organoaluminium compounds[477] react with $Me_2NPCl_2$ and $(Me_2N)_2PCl$ giving dialkylphosphinous dimethylamide and monoalkylphosphonous tetramethyldiamide respectively. These compounds are cleaved by anhydrous hydrogen chloride[68, 334, 336] or with phosphorus trichloride[477] to the corresponding chlorides:

$$Me_2NPCl_2 \xrightarrow{2RMgX} Me_2NPR_2 \xrightarrow{HCl} R_2PCl + Me_2NH,HCl$$
$$(Me_2N)_2PCl \xrightarrow{RMgX} (Me_2N)_2PR \xrightarrow{HCl} RPCl_2 + 2Me_2NH,HCl$$
$$Et_2NPCl_2 \xrightarrow{AlEt_3} Et_2NPEt_2 \xrightarrow{PCl_3} Et_2PCl + Et_2NPCl_2$$

Diazoalkanes react with phosphorus trichloride giving by progressive substitution $RCH(Cl)PCl_2$, $[RCH(Cl)]_2PCl$ and $[RCH(Cl)]_3P$.[535] The use of diazo compounds in organophosphorus chemistry is reviewed briefly by Seyferth.[536] Esters of alkyl and aryl phosphonochloridous acid can be prepared in good yield by coproportionation of the diester and phosphonous dichloride[544]:



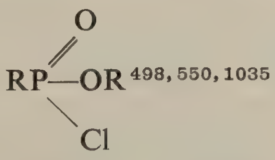
$$RPCl_2 + RP(OR'_2) \rightarrow 2RP\begin{matrix} Cl \\ OR' \end{matrix}$$

Typical reactions of phosphonous dihalides are shown in Chart VIII.

The photochemical or peroxide-catalyzed addition of phosphorus trichloride and phosphorus tribromide to olefines affords moderately good yields of 2-halogen substituted phosphonous dichloride.[2395–7] The peroxide catalyzed reaction of octene-1 and phosphorus trichloride is said to yield a single product, 2-chloro-octyl phosphonous dichloride.[2395] The ultra-violet catalyzed reaction of propylene and phosphorus tribromide gives almost pure $CH_3CH(PBr_2)CH_2Br$ but the thermal reaction at 150° gives a mixture of 70% $CH_3CH(PBr_2)CH_2Br$ and 30% $CH_3CHBr.CH_2PBr_2$.[2397]

### Phosphonyl Dihalides ($RPOX_2$) and Phosphinyl Halides ($R_2POX$)

These compounds are generally liquids or solids having low melting points. The chlorides, bromides, and iodides are readily hydrolyzed by water; in contrast, fluoro compounds are more stable and phenylphosphonic difluoride is reported not to be hydrolyzed in boiling water.[381] Compounds of the type $RPSF_2$ are more stable to hydrolysis than the corresponding oxygen compounds $RPOF_2$, whilst $R_2PA.F$ ($A = O, S$) are generally more stable than $RPA.F_2$.[547] The kinetics of hydrolysis of several phosphinyl chlorides[498, 550, 1035] and fluorides[438, 549, 1176] and of phosphonyl dichlorides[1035] have been determined, as have the kinetics of hydrolysis of *O*-alkyl phosphonochloridates:



$$RP\begin{matrix} O \\ —OR \\ Cl \end{matrix}$$ [498, 550, 1035]

and their reactions with amines to form *N*-substituted phosphonamidate esters.[551]

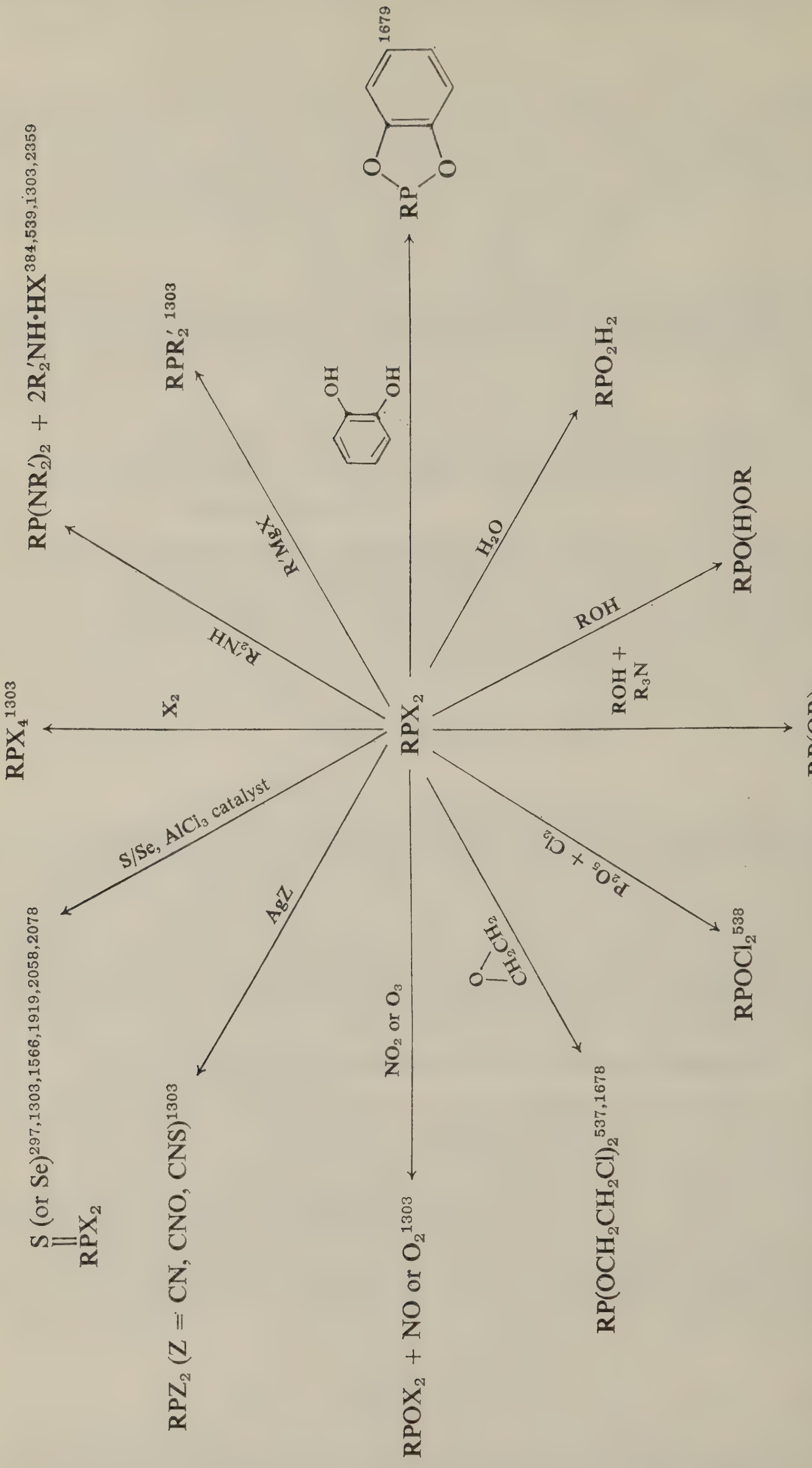


CHART VIII.—Reactions of phosphonous dihalides, $RPX_2$

**Ref. p. 1082**

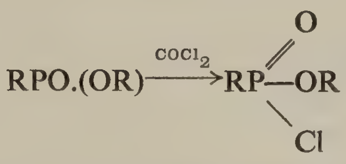
The densities, viscosities, molar polarization, dipole moments, refractive indices, vapour pressures, freezing points, and infra-red spectra of $MePOCl_2$, $Me_2POF_2$, and MePOFCl have been obtained.[1450] The nuclear magnetic resonance[384, 552] of alkylphosphonyl dichlorides, alkylarylphosphinyl chlorides and the corresponding acids and esters have been examined. Heats of formation and bond energies in $MePOCl_2$, $EtPOCl_2$, and their corresponding acids and ethyl esters have been evaluated.[1327] Phosphonic halides form complexes with metal halides such as $AlCl_3$, $BF_3$, $BCl_3$, $TiCl_4$, $SbCl_5$ and $SnCl_4$.[2367]

### PREPARATION FROM ESTERS OR ACIDS BY HALOGENATION

Phosphonic or phosphinic acids or their esters, and aromatic phosphinothioic acids[359] are readily converted to the corresponding phosphonyl and phosphinyl chlorides by treatment with reagents such as phosphorus pentachloride or thionyl chloride[358]:

$$\begin{array}{c} RPO.(OR')_2 \xrightarrow[\text{or } SOCl_2]{PCl_5} RPOCl_2 \xleftarrow{PCl_5} RPO_3H_2 \\ R_2PO.OR \longrightarrow R_2POCl \longleftarrow R_2PO_2H \end{array}$$

By judicious treatment of dialkylphosphonates with reactive chlorides such as $PCL_5$, $SOCl_2$,[353] $COCl_2$[354] or $(COCl)_2$,[353] it is possible to obtain high yields of *O*-alkyl phosphonochloridates:

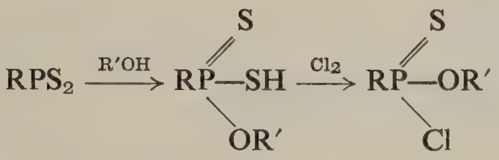


$$RPO.(OR) \xrightarrow{COCl_2} RP(=O)(-OR)(-Cl)$$

The mechanism of the reaction of pentavalent phosphorus esters with phosgene has been investigated by Green and Hudson who showed that the reaction rate decreased in the series:

$$R_2PO.OMe > ROPR'O.OMe > (RO)_2PO.OMe^{543}$$

*O*-Alkyl and *O*-aryl phosphonochloridothionates[356–7] can be obtained from thionophosphine sulphides by treatment with alcohol or phenol followed by chlorination:



$$RPS_2 \xrightarrow{R'OH} RP(=S)(-SH)(-OR') \xrightarrow{Cl_2} RP(=S)(-OR')(-Cl)$$

Aromatic phosphinodithioic acids yield diaryl phosphinochloridothionates by treatment with hydrogen chloride[328]:

$$Ar_2PS_2H + HCl \rightarrow Ar_2PSCl + H_2S$$

### FROM PHOSPHONOUS AND PHOSPHINOUS HALIDES BY ADDITION OF OXYGEN, SULPHUR OR SELENIUM

In common with other compounds containing trivalent phosphorus, phosphonous dihalides and phosphinous halides react with oxygen,[185] sulphur[357, 1303] or selenium,[169, 1303] giving the corresponding phosphonic or phosphinic, phosphonothionic or phosphinothioic, phosphonoselenoic or phosphinoselenoic[428] halides.

Phosphinous chlorides oxidize more readily than phosphonous dichlorides which usually oxidize readily only when free from impurities. A catalyst such as aluminium chloride is frequently used to effect the addition of sulphur[361] or selenium.[2058]

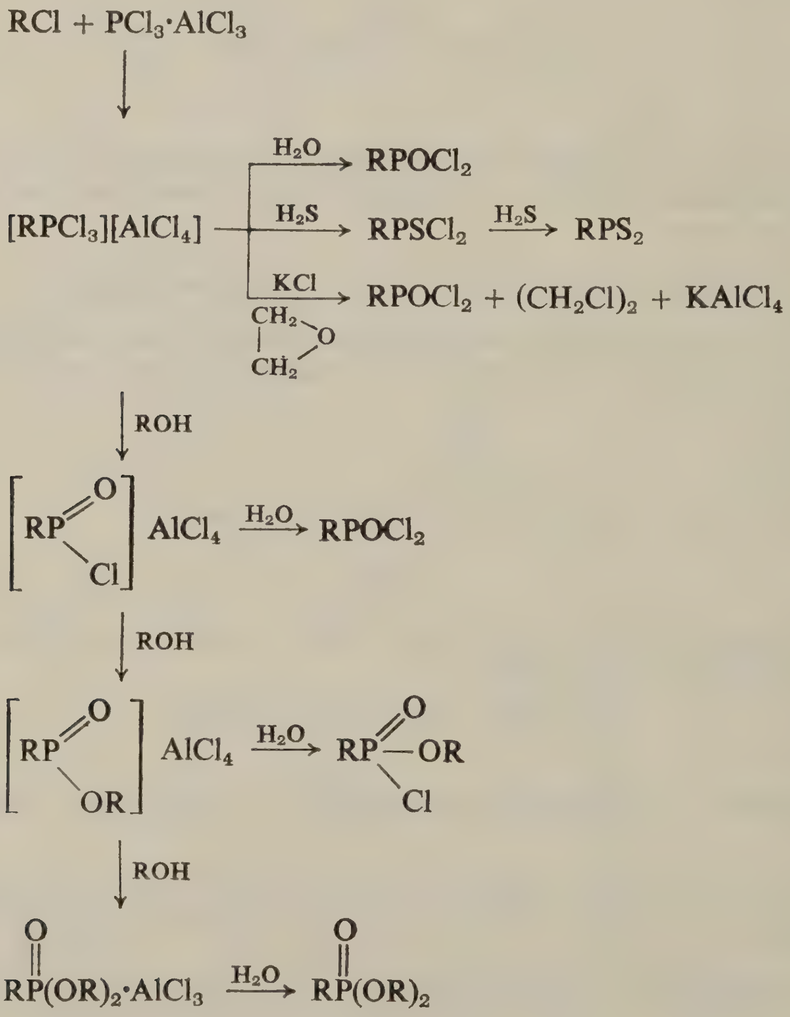
Phosphorus pentasulphide has been used to convert phosphonyl and phosphinyl chlorides into their thio analogues[362, 546, 1680]:

$$RPOCl_2 \xrightarrow{P_2S_5} RPSCl_2$$

The oxidation of $PhPCl_2$ and $Ph_2PCl$ to $PhPO.Cl_2$ and $Ph_2PO.Cl$ respectively, using sulphur dioxide and phosphorus tribromide catalyst, is reported.[1681] Benzyl- and phenylphosphonous dihalides are readily oxidized to the corresponding phosphonic dihalides with dry oxides of nitrogen.[2057] Equilibrium studies on reactions of the type $MePSCl_2 + POCl_3 \rightleftharpoons MePOCl_2 + PSCl_3$ have been carried out by Groenweghe and Payne.[545]

### PREPARATION FROM KINNEAR–PERREN[320] COMPLEXES

Phosphorus trichloride, alkyl halide and aluminium chloride react together to give a complex (an alkyltrichlorophosphonium tetrachloroaluminate) which is hydrolyzed by careful addition of water[320, 363] giving alkylphosphonyl dichloride. Treatment with hydrogen sulphide,[320] sulphur,[2364] potassium thiocyanate[2364] or alkylene sulphide[2363] gives alkylphosphonothionic dichloride. Treatment with alcohols can be adjusted to give the phosphonyl dichloride,[440] the alkyl phosphonochloridate[440] or the phosphonic diester.[440] Alkylene oxides react with the complexes at low temperature in the presence of potassium chloride to form phosphonic dichlorides and 1,2-dichloroalkene[350, 2363]:



Isomerization[541] and degradation occur with some alkyl groups. Thus, *n*-propyl and *n*-butyl chlorides give *iso*propyl and *sec*-butyl phosphonyl dichlorides[320];

*tert*-amyl chloride gives a mixture of *tert*-butyl and *tert*-amylphosphonyl dichlorides[364]; 2-chloro-2,3-dimethylbutane gives predominantly *tert*-butylphosphonyl dichloride.[542] 1-Halogeno-2-alkyl alkanes give tertiary phosphonyl dichlorides.[320, 540]

Similar complexes, $[RR'PCl_2][AlCl_4]$ are formed from phosphonous dichlorides. They are decomposed by water[356] to the phosphinyl chloride, by sulphur or a sulphide (of aluminium, phosphorus, antimony or arsenic) to phosphinothioic chlorides,[365] and by alcohol to the phosphinic acid ester.[439]

### PREPARATION BY OXIDATIVE PHOSPHONYLATION

Aliphatic hydrocarbons[366-7, 371, 2366] and substituted aliphatic hydrocarbons[368] react with phosphorus trichloride and oxygen to yield phosphonyl dichlorides. The overall reaction may be represented by the equation:

$$RH + PCl_3 + \tfrac{1}{2}O_2 \rightarrow RPOCl_2 + HCl$$

The yield of phosphonyl dichloride is generally poor and much of the phosphorus trichloride is simply oxidized to phosphorus oxychloride. Studies of the factors influencing the yield of phosphonic dichloride have been made by Isbell and Wadsworth,[370] by Pianfetti and Quin,[383] and by Mayo and co-workers.[555] The mechanism of the reaction is discussed by Flurry and Boozer.[2365] Many catalytic reagents[369, 370] have been used without success in attempts to improve the yield of phosphonyl dichloride. Single products are obtained only from hydrocarbons such as methane,[383] ethane,[367, 383] and *cyclo*hexane,[366] in which all the hydrogen atoms are equivalent; in other cases mixtures of all the possible isomers result.[371] 1-Chlorobutane gives the 1-, 2-, 3-, and 4-phosphonyl dichlorides in the following ratios: 9·5:20·5:54:16.[368]

Olefines[372-3] and acetylenes[374] yield 2-chloroalkyl- and 2-chloroalkenylphosphonyl dichlorides respectively. The products correspond to those expected for the free radical addition of phosphorus trichloride and phosphorus oxychloride to the double or triple bond. Phosphinyl chlorides have been obtained by using phosphonous dichlorides in place of phosphorus trichloride[375-6, 1302, 1325]:

$$RPCl_2 + R'H \xrightarrow{PCl_3/O_2} RR'POCl + HCl$$

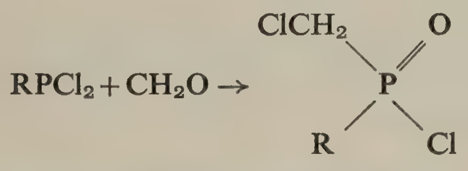
### FROM PHOSPHOROUS HALIDES AND ALDEHYDES

Formation of 1-chlorophosphonyl dichlorides by the high temperature reaction of phosphorus trichloride with aldehydes and ketones is a general reaction with few exceptions.[377] With most aromatic aldehydes[378] and formaldehyde[379] the reaction proceeds well but other aliphatic aldehydes give poor yields. Formaldehyde and phosphorus trichloride yield chloromethylphosphonyl dichloride:

$$CH_2O + PCl_3 \xrightarrow[3\text{ hr.}]{250°} ClCH_2POCl_2$$

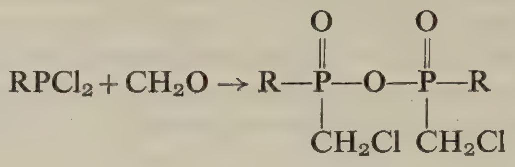
Small amounts of $ClCH_2PO.(CH_2Cl)Cl$ and $ClCH_2PO.(CH_2Cl)_2$ have been isolated as by-products.[379]

Similar reactions occur at high temperatures between aliphatic and aromatic phosphonous dichlorides and formaldehyde to give chloromethylphosphinyl chlorides[380]:



Diphenylphosphinous chloride and formaldehyde form chloromethyldiphenylphosphine oxide.[380]

Alkyl and aryl phosphonous dihalides and paraform react at moderate temperatures giving good yields of chloromethyl phosphinic acid anhydrides[562]:



$$RPCl_2 + CH_2O \rightarrow R{-}\overset{\overset{O}{\|}}{\underset{\underset{CH_2Cl}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{CH_2Cl}{|}}{P}}{-}R$$

MISCELLANEOUS METHODS

Alkylation of thiophosphorus halides such as $PSCl_3$, $PSBr_3$, $RPSCl_2$, $(EtO)_2PSCl$, and $(Me_2N)_2PSCl$ by organoaluminium compounds has been studied by Maier.[1304]

Mixtures of phenylphosphonothioic dichloride, diphenylphosphinothioic chloride and triphenylphosphine sulphide are formed by the aluminium trichloride catalyzed reaction of thiophosphoryl chloride with benzene.[1749] The yield and product composition are determined by the molar ratio of the reactants, reaction time, and temperature. Di-(*tert*-butyl)phosphinic chloride has been obtained by the reaction[437]:

$$\text{P(white)} + Me_3CCl\ (1) \xrightarrow[\text{CS}_2\text{ solution}]{\text{AlCl}_3} (2) \xrightarrow[\text{hydrolysis}]{\text{Oxidative}} (Me_3C)_2POCl$$

Phosphonyl difluorides, phosphonothioic difluorides[381] and phosphinyl fluorides[382, 438] have been obtained from the corresponding chlorides by treating with fluorinating agents such as zinc fluoride,[381] hydrogen fluoride,[382] sodium fluoride[438] or potassium fluorosulphinate,[547] and by partial hydrolysis of tetrafluorophosphoranes.[547] Methylphosphonous dichloride reacts with potassium fluorosulphinate giving a mixture of methylphosphonic difluoride and methylphosphonothioic difluoride; similarly dimethylphosphinous chloride gives dimethylphosphinic fluoride and dimethylphosphinothioic fluoride.[547] Diphosphine disulphides and dialkylphosphinothioic chlorides react with thionyl chloride giving good yields of dialkylphosphinyl chlorides.

Phosphonothioic dihalides may be prepared by the thermal rearrangement of phosphorodihalogenidothioites:

$$RSPCl_2 \xrightarrow{\Delta} RP(S)Cl_2 \qquad (R = \text{alkyl, allyl, phenyl})$$

The rearrangement is catalyzed by iodine, methyl iodide or iodine salts and occurs at 135°–165° when R = allyl and 275°–400° when R = methyl.[2368] Methylphosphonyl dichloride can be produced by pyrolysis of dimethyl phosphite at 250°C., followed by chlorination with phosgene.[2430]

## Halogenophosphoranes

Chlorine combines with phosphonous dichlorides and phosphinous chlorides to form tetrachlorophosphoranes and trichlorophosphoranes respectively. The reactions are exothermic and are generally conducted in inert solvents. The products, yellow crystalline solids which generally resemble phosphorus pentachloride in appearance and reactivity, are isolated by filtration. A few mixed chlorobromophosphoranes have been prepared[1] by the addition of bromine to phosphonous dichlorides or phosphinous chlorides. Chlorophosphoranes are frequently prepared by chlorination of phosphonic[342] or phosphinic[341] acids and their chlorides or esters with phosphorus pentachloride:

$$RPCl_2 \xrightarrow{Cl_2} RPCl_4 \xleftarrow{PCl_5} RPO_3H_2$$
$$R_2PCl \xrightarrow{Cl_2} R_2PCl_3 \xleftarrow{PCl_5} R_2PO_2H$$

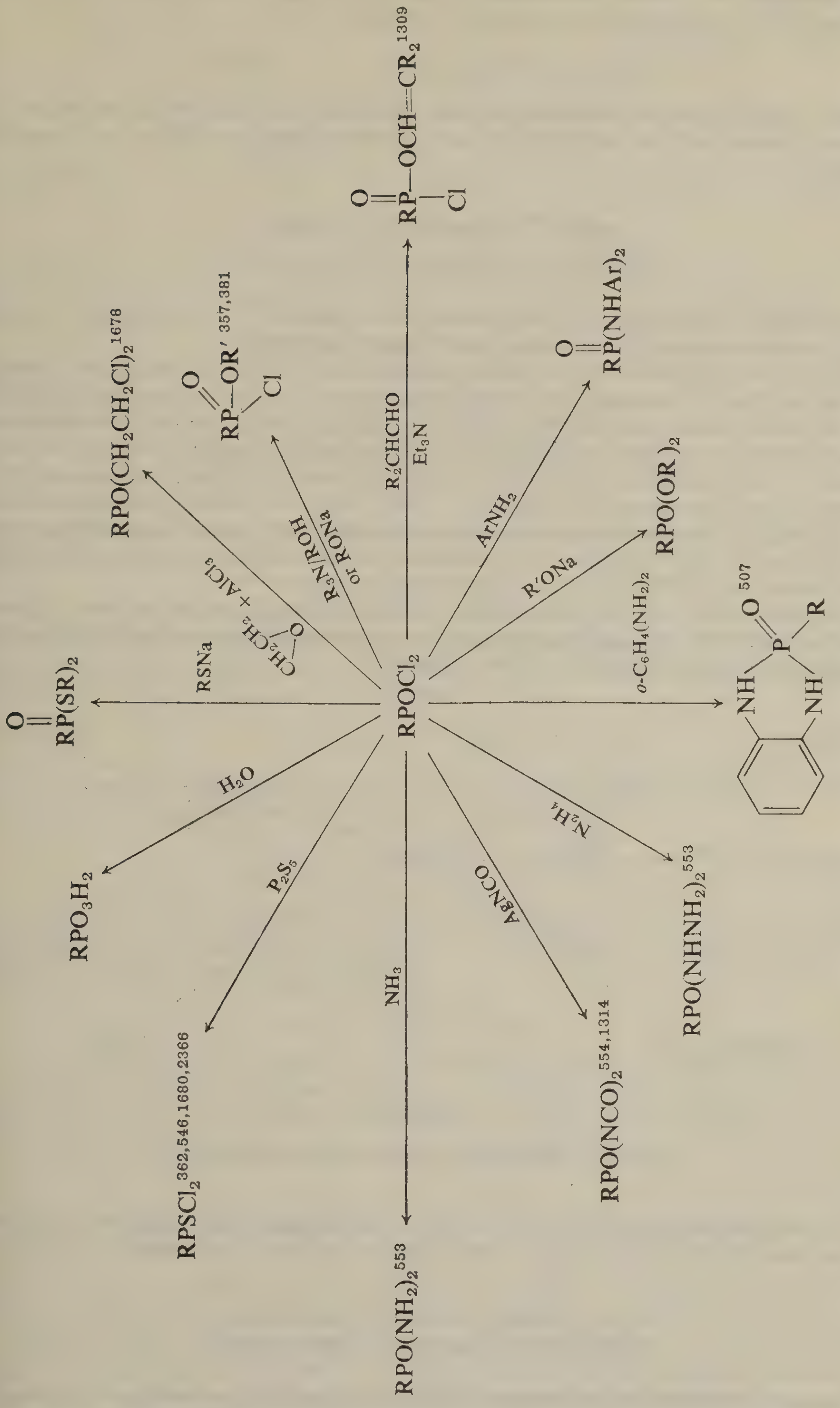


CHART IX.—Some typical reactions of phosphonodichlorides *cyclo*Hexylphosphorane tetrabromide and tetraiodide are formed in good yield by halogenation of tetra*cyclo*hexyltetraphosphine; tetra*cyclo*hexyldiphosphine similarly yields the di*cyclo*hexylphosphorane trihalides[1886]:

$$(C_6H_{11}P)_4 \xrightarrow{X_2} C_6H_{11}PX_4 \qquad (X = Br, I)$$

Mono- and di-phenylchlorophosphoranes are readily obtained by chlorination of phenylthionophosphine sulphide[338] and diphenylphosphinodithioic acid respectively:

$$PhPS_2 \xrightarrow{Cl_2} PhPS.Cl_2 \xrightarrow{Cl_2} PhPCl_4$$
$$Ph_2PS_2H \xrightarrow{Cl_2} Ph_2PS.Cl \xrightarrow{Cl_2} Ph_2PCl_3$$

Diphosphine disulphides are halogenated with chlorine[561] or bromine[561] giving trichlorophosphorane and tribromophosphorane respectively.

Crystalline compounds having the composition $R_3PX_2$ ($X = Cl, Br, I$) are formed by the addition of halogens to tertiary phosphines. The compounds are insoluble in non-polar media but soluble in solvents such as acetonitrile and nitrobenzene. Formulation as ionic solids, $[R_3PX]^+X^-$ (halogenophosphonium halides), is indicated by their solubility behaviour, by their high melting points, by electrical conductivity in nitrobenzene solution,[144] and from infra-red spectroscopy of $(CH_3)_3PX_2$.[1019] By mixing dihalogenophosphoranes with metal halides of the type $MX_n$ ($M = Sb^V, Sb^{III}, Hg^{II}$) in nitrobenzene solution, double salts, probably of ionic structure $[R_3PX]^+[MX_{n+1}]^-$, have been obtained.[144]

Pseudohalogens such as cyanogen bromide and triphenylphosphine react to form $Ph_3P,CNBr$.[16, 1987] Typical reactions of tetrachlorophosphoranes and dihalogenophosphoranes are indicated in Charts X and XI.

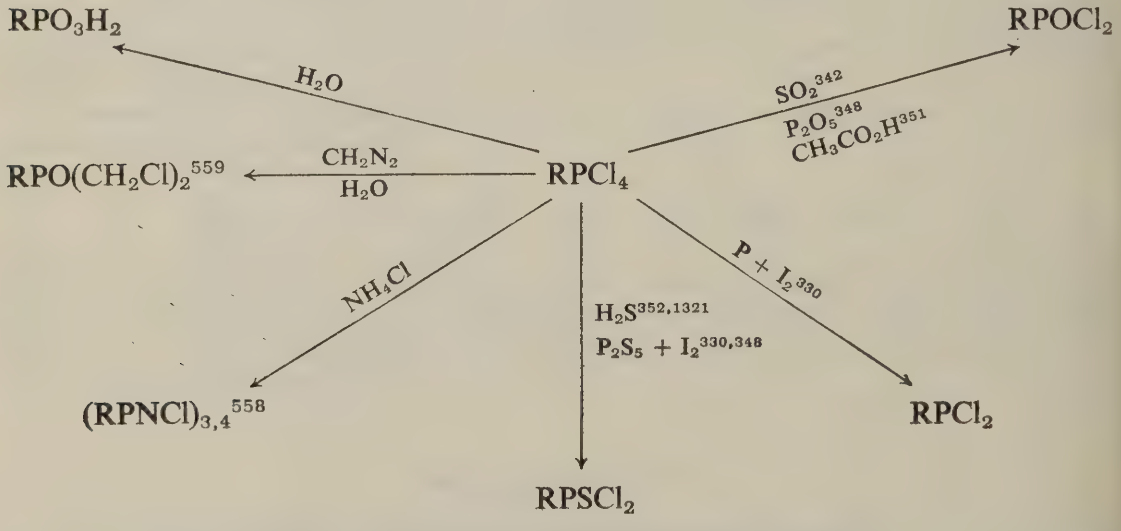


CHART X.—Reactions of tetrachlorophosphoranes

Fluorophosphoranes $R_nPF_{5-n}$ ($n = 1$ or 2) are obtained by fluorination of chlorophosphines $R_nPCl_{3-n}$ ($n = 1$ or 2) with arsenic or antimony trifluoride[302, 340, 556, 891, 991]:

$$3RPCl_2 + 4MF_3 \rightarrow 3RPF_4 + 2M + 2MCl_3$$
$$3R_2PCl + 3MF_3 \rightarrow 3R_2PF_3 + 2M + MCl_3$$

Antimony pentafluoride has been used similarly[339] and for the conversion of phenylphosphonous difluoride to phenyltetrafluorophosphorane.[339] Phenylfluorophosphoranes $Ph_nPF_{5-n}$ ($n = 1, 2, 3$) are obtained by replacing oxygen by fluorine in

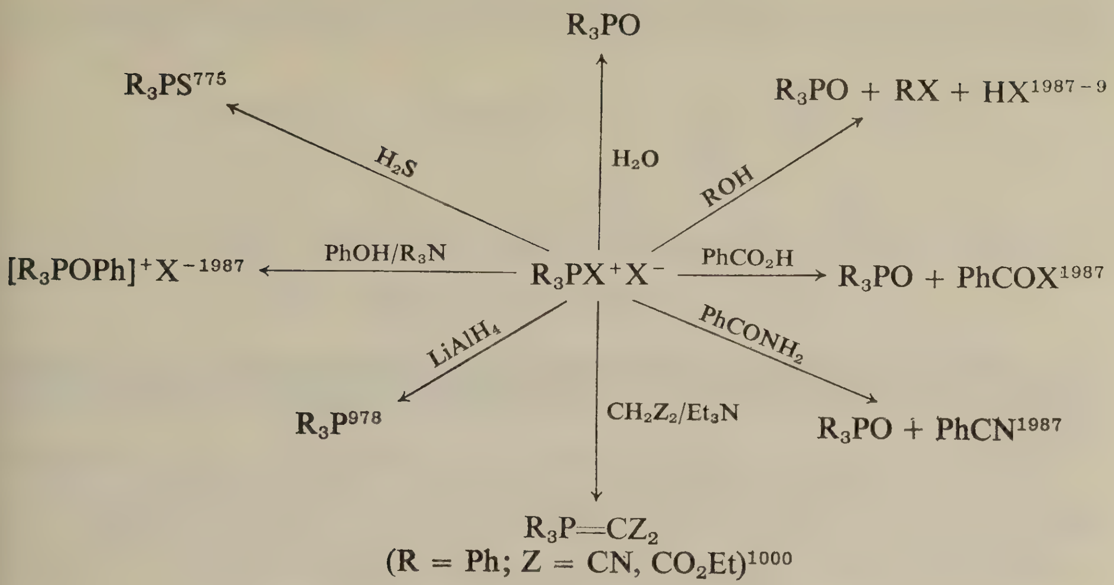


CHART XI.—Reactions of dihalogenophosphoranes

appropriate pentavalent phenylphosphorous compounds using sulphur fluoride,[775] e.g.,

$$Ph_3PO \xrightarrow{SF_4} Ph_3PF_2$$

Pentavalent phosphorus compounds containing sulphur, e.g. tributylphosphine sulphide and tetra-alkylphosphine disulphides, are readily converted to fluorophosphoranes by the use of antimony trifluoride[981, 1941]:

$$Bu_3PS \xrightarrow{SbF_3} Bu_3PF_2$$

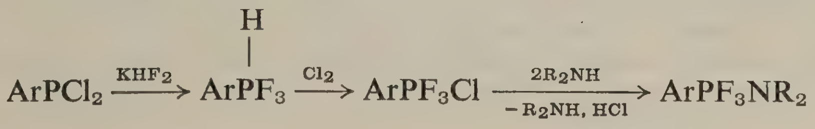
Fluorination of triphenylphosphine and diphenylphosphine with tetrafluorohydrazine affords the corresponding fluorophosphoranes[2063]:

$$2Ph_3P + N_2F_4 \rightarrow 2Ph_3PF_2 + N_2$$
$$Ph_2PH + N_2F_4 \rightarrow Ph_2PF_3 + N_2 + HF$$

Kinnear–Perren complexes $RPCl_3.AlCl_4$ and $R_2PCl_2.AlCl_4$ are converted to fluorophosphoranes by treatment with hydrogen fluoride,[892] alkali metal fluorides and antimony or arsenic trifluorides,[891] e.g.,

$$MePCl_3.AlCl_4 \xrightarrow{HF} MePF_4$$

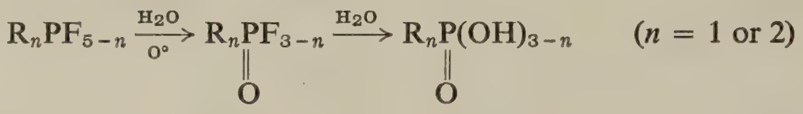
Arylphosphonous dichlorides and potassium hydrogen fluoride react to form aryltrifluorohydrogenphosphoranes which can be chlorinated to arylchlorotrifluorophosphoranes.[560] The chlorine atom in these compounds is selectively replaced on reaction with amines:



$$ArPCl_2 \xrightarrow{KHF_2} \overset{\displaystyle H \atop |}{ArPF_3} \xrightarrow{Cl_2} ArPF_3Cl \xrightarrow[-R_2NH,\ HCl]{2R_2NH} ArPF_3NR_2$$

Alkyltetrafluorophosphoranes are formed by the action of phosphorus pentafluoride on tetra-alkyltin compounds at room temperature.[2064]

Fluorophosphoranes are generally colourless liquids which are stable to distillation. Tetrafluorophosphoranes have boiling points about 80°C. below those of the corresponding dichlorophosphines; trifluorophosphoranes have boiling points about 20° below those of the monochlorophosphines[991]; methyl tetrafluorophosphorane is a gas, b.p. 10°C. They are readily hydrolyzed, the first step being production of the phosphonic or phosphinic fluoride which, under more vigorous conditions, gives the corresponding acids:



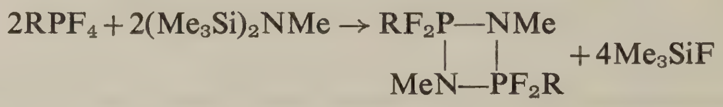
$$R_nPF_{5-n} \xrightarrow[0^\circ]{H_2O} R_nP(=O)F_{3-n} \xrightarrow{H_2O} R_nP(=O)(OH)_{3-n} \qquad (n = 1 \text{ or } 2)$$

The hydrolytic stability of di- and trifluorophosphoranes decreases in the order:

$$R_3PF_2 > R_2ArPF_2 = Ar_2PF_3 \gg R_2PF_3{}^{1941}$$

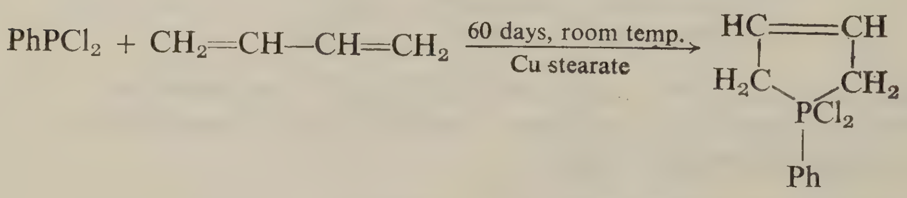
Tributyldifluorophosphorane is indefinitely stable in glass apparatus without special protection from moisture while triphenyldifluorophosphorane undergoes rapid hydrolysis.

Phosphorus fluorides such as $PF_5$, $RPF_4$, and $R_2PF_3$ react with hexamethyldisiloxane with cleavage of the Si–O bond, the products being $Me_3SiF$ and $POF_3$, $RPOF_2$, or $R_2POF$, respectively.[1564] With heptamethyldisilazane products are formed which contain a fluoro-1,3,2,4-diazadiphosphetidine ring system,[1529] e.g.,



HALOGENOPHOSPHORANES FORMED BY REACTIONS INVOLVING P–C BOND FORMATION

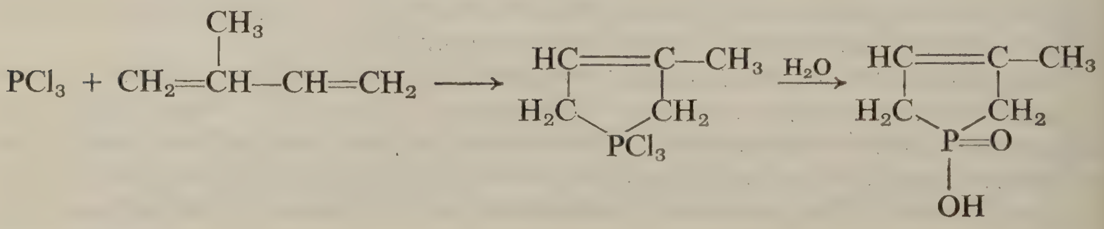
Cyclic chlorophosphoranes (P-substituted phospholine derivatives) are formed by the Diels-Alder type of reaction between phosphonous dichlorides and 1,3-dienes. The reaction is generally conducted at ambient temperatures in the presence of a polymerization inhibitor such as copper stearate or an aromatic polynitro compound.[951, 1912, 2369]



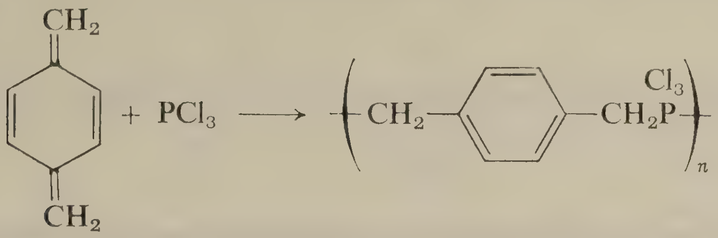
1-Phenyl-3-phospholene-1, 1-dichloride

The oxides derived from the dichlorides by hydrolysis possess high activity as catalysts for the formation of carbodi-imides from *iso*cyanates.[237, 1878, 1893, 1904, 1906]

Similar reactions are reported between dienes and phosphorus trichloride or tribromide to form 1,1,1-trihalogenophospholene derivatives[1001, 1006] and with phenylphosphorodichloridite[951] giving a *P*-phenoxydichlorophospholene:



*p*-Xylylene and trivalent phosphorous halides, e.g., the series $PCl_3$, $PhPCl_2$, and $Ph_2PCl$, react to form interesting polymeric halogenophosphoranes[343]:

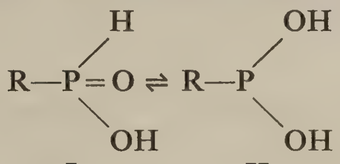


Nitriles such as acetonitrile, chloroacetonitrile and dichloroacetonitrile and phosphorus pentachloride react[557] as follows:

$$NCCHX_2 + 2PCl_5 \rightarrow NCCX_2PCl_4,PCl_5 + HCl \qquad (X = Cl \text{ or } H)$$

## Phosphonous Acids and Their Esters

The chemistry of phosphonous acids has been reviewed by Frank.[388] Phosphonous acids are monobasic acids and have been shown by nuclear magnetic resonance,[3] infra-red[3] and ultra-violet[387] spectroscopy to have the general structure **I.** As in related classes of compounds the possibility of a tautomeric equilibrium with a tricovalent form **II** has been considered, but form **I** is the overwhelmingly predominant species[3, 389]:



**I** **II**

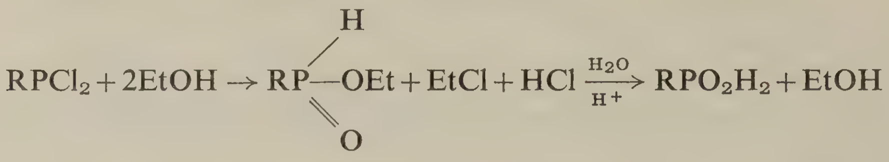
The hydrogen atom attached to phosphorus in phenylphosphonous acid, like that in $H_3PO_3$ and in diethyl hydrogen phosphate, undergoes isotopic exchange with deuterium in $D_2O/H_2O$ solution, probably *via* the formation of an intermediate of structure **II.** The relative rates of deuterium exchange of the three compounds are given by Reuben *et al.*[565] Trimeric association of phenylphosphonous acid in benzene solution has been described by Kosolapoff and Powell.[390]

Most aliphatic members are liquids which, due to disproportionation, cannot be purified by distillation; aromatic members are usually solids which are readily purified by crystallization. The $pK_a$ values of several aromatic phosphonous acids have been determined[385]; phenylphosphonous acid has $pK_a$ 1·75 at 25° in water. Methylphosphonous acid has $pK = 2{\cdot}3$, and proton magnetic resonance indicates structure **I.**[564] Trifluoromethylphosphonous acid has an acid dissociation constant, $K = 9{\cdot}8 \times 10^{-2}$; its infra-red spectrum is also in accordance with structure **I.**[563]

The acids are in general stable to atmospheric oxidation but are oxidized by a wide variety of mild oxidizing agents.[388] They form two series of derivatives; mono-derivatives RPH(O)Y, and di-derivatives $RP(Y)_2$, derived from the two isomeric forms **I** and **II.**

### PREPARATION

The most convenient and general method of obtaining phosphonous acids is hydrolysis of the corresponding phosphonous dihalide. These are rapidly hydrolyzed by ice-cold water[2356] or concentrated hydrochloric acid[330] often forming some phosphonic acid and phosphine by disproportionation. The best method is hydrolysis by addition to aqueous ethanol[390] or methyl alcohol[564]:



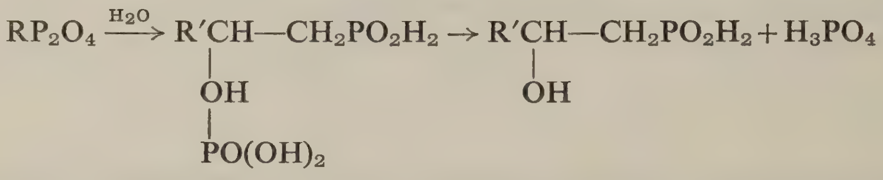
$$RPCl_2 + 2EtOH \rightarrow \underset{\diagdown O}{\overset{H \diagup}{RP}}\!\!-\!OEt + EtCl + HCl \xrightarrow[H^+]{H_2O} RPO_2H_2 + EtOH$$

Glassy polymeric phenylphosphonous anhydrides are reported to form by the action of water on phenylphosphonous dichloride or tetramethyl phenylphosphonous diamide. The analogous thio anhydride is obtained from the chloro compound and hydrogen sulphide[2373]; it reacts with bromine giving phenylphosphonothionic dibromide:

$$PhPCl_2 + H_2O \xrightarrow{-2HCl} (PhPO)_7 \xleftarrow{-2Et_2NH} PhP(NEt_2)_2 + H_2O$$
$$PhPCl_2 + H_2S \xrightarrow{-2HCl} (PhPS)_5 \xrightarrow{Br_2} PhPSBr_2$$

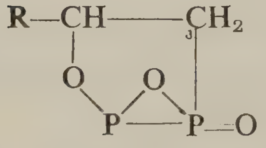
Other methods of preparation, generally of much narrower application, are outlined below.

Olefins react with white phosphorus and oxygen in inert solvents[391] giving crystalline 'phosphorates' (Willstätter) of empirical formula $RP_2O_4$ which are hydrolyzed by water to 2-hydroxyalkylphosphonous acids. More often the phosphorates have been treated with nitric acid to obtain phosphonic acids. Olefins which give soluble 'phosphorates' react further with oxygen giving compounds of empirical formula $RP_2O_5$[392]:

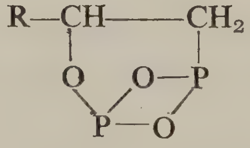


$$RP_2O_4 \xrightarrow{H_2O} \underset{\underset{PO(OH)_2}{|}}{\underset{OH}{\underset{|}{R'CH}}}\!-\!CH_2PO_2H_2 \rightarrow \underset{OH}{\underset{|}{R'CH}}\!-\!CH_2PO_2H_2 + H_3PO_4$$

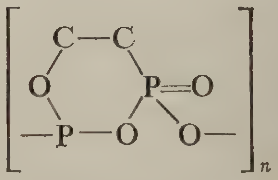
In a related reaction, olefins, phosphorus trichloride and acetic anhydride react to give crystalline 'phosphorites' $RP_2O_4$[393] (Stayner) which are hydrolyzed to $\alpha$-$\beta$ unsaturated phosphonous acids. The proposed structures of the 'phosphorates' and 'phosphorites' together with a polymeric structure suggested by Walling *et al.*[392] are given below:



Wilstätter

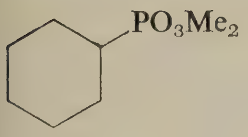


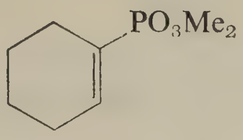
Stayner

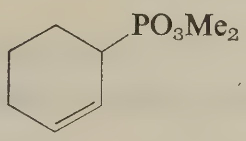


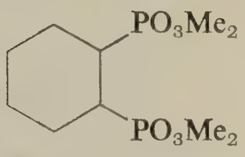
Walling

Recent work by Eckert *et al.*[2394] suggests that the structure of these compounds could be more complex than any of those indicated above with at least some components having two P–C bonds. A number of olefins were converted to the complexes [olefin, $P_2O_n$] (where $n = 4$–5) by reaction with white phosphorus and oxygen. The molecular weight of the octene complex corresponds to a pentamer with $n = 5$, i.e. $[C_8H_{15}P_2O_5]_5$. Hydrolysis of this followed by methylation with diazomethane yielded a mixture of trimethyl phosphate, dimethyl octene phosphonate and tetramethyl octane diphosphonate. The *cyclo*hexene adduct was converted with phosphorus pentachloride to a mixture of phosphonic chlorides and hence to the methyl esters indicated below:









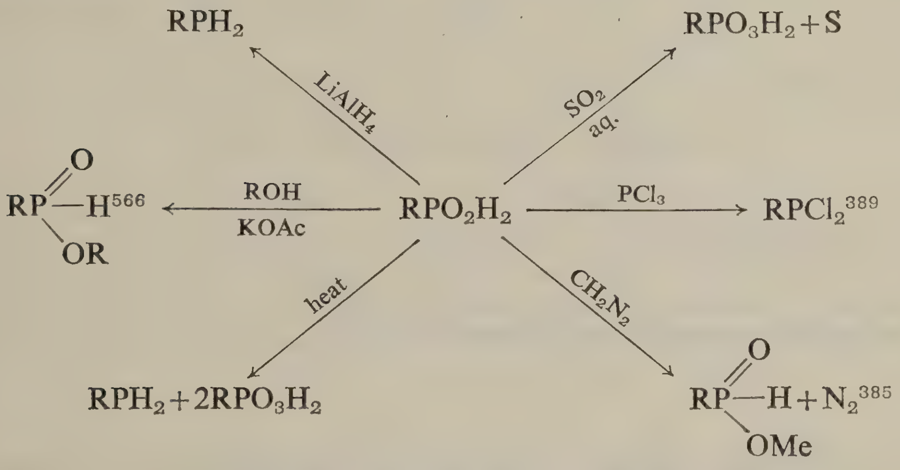
Hypophosphorous acid adds to carbonyl compounds giving $\alpha$-hydroxyalkylphosphonous acids[394] and undergoes a Mannich type of reaction with Schiff's bases forming *N*-substituted-$\alpha$-aminoalkylphosphonous acids.[395] When aldehydes or acetone are used in the reaction the initially formed phosphonous acid may undergo further condensation giving bis($\alpha$-hydroxyalkyl)phosphinic acid[396, 2376]:

$$RCHO + H_2PO_2H \rightarrow RCHOH.PH.O_2H \xrightarrow{RCHO} (RCHOH)_2PO_2H$$

Addition to dialkyl maleate gives a 1,2-dicarbalkoxyethylphosphonous acid.[1324] Sodium hypophosphite adds to olefines in the presence of free-radical initiators to give the sodium salts of a phosphonous acid which can undergo further addition to olefine giving a sodium dialkylphosphinate[397]:

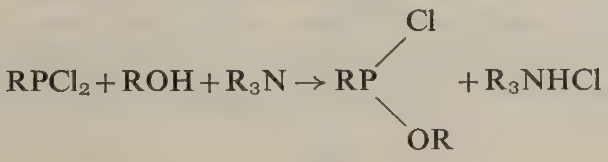
$$RCH{=}CH_2 + H_2PO_2Na \rightarrow RCH_2{-}CH_2PH.O_2Na \rightarrow (RCH_2CH_2)_2PO_2Na$$

Aryldiazonium compounds are said to react with sodium hypophosphite in the presence of copper sulphate giving arylphosphonous acids.[442] Potassium salts of acyl phosphonous acids ($\alpha$-ketoalkylphosphonous acids) are formed by the action of acyl anhydrides on $KH_2PO_2$.[1310] Some typical reactions of phosphonous acids are shown below.

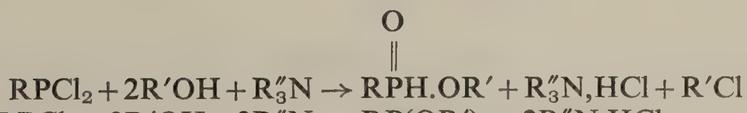


ESTERS OF PHOSPHONOUS ACIDS

The reactions of phosphonous dichlorides with alcohols in the presence of appropriate amounts of tertiary amine to give alkyl phosphonochloridites,[410] and mono[398] and dialkyl phosphonites[399, 423] are shown below:



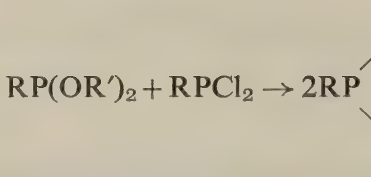
$$RPCl_2 + ROH + R_3N \rightarrow RP\begin{matrix} \diagup Cl \\ \diagdown OR \end{matrix} + R_3NHCl$$



$$RPCl_2 + 2R'OH + R''_3N \rightarrow \overset{\displaystyle O}{\overset{\|}{RPH}}.OR' + R''_3N,HCl + R'Cl$$

$$RPCl_2 + 2R'OH + 2R''_3N \rightarrow RP(OR')_2 + 2R''_3N,HCl$$

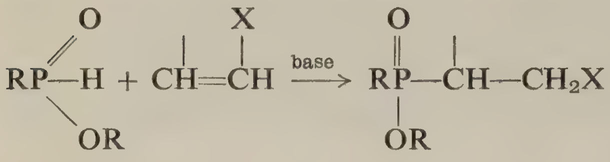
Sodium alkoxide[400] or ammonia[401] has been used in place of tertiary amine. Diesters from phenols[402] are not 'dearylated' by hydrogen chloride and can be prepared by heating the phosphonous dichloride and phenol together. The intermediate phosphonochloridous esters have been prepared indirectly by the reaction[544]:



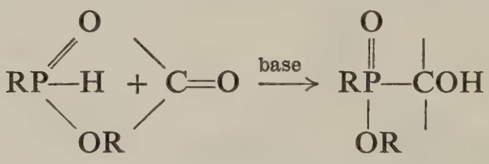
(R = alkyl, aryl)

The mono- and dialkyl esters are liquids which can generally be distilled under reduced pressure without decomposition. They undergo many reactions which are analogous to those known for dialkyl hydrogen phosphonates and trialkyl phosphites but generally exhibit a greater degree of reactivity.

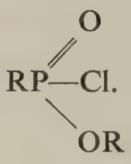
The mono-esters may also be prepared by direct esterification of phosphonous acids.[566] They form salts RPO.ORNa by treatment with sodium in anhydrous media. These add sulphur giving salts of alkylphosphonothionic acid,[404] and react with alkyl halides[405] giving alkyl phosphinates. The esters undergo many base-catalyzed addition reactions, adding in the sense RPO.OR···H, to activated olefins,[398, 406] Schiff's bases,[407] and carbonyl compounds,[407] to give alkyl phosphinates:



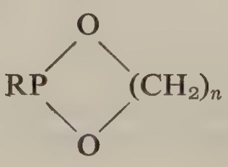
(X = —C=O, —CO$_2$R, —CN, —PO(OR)$_2$)



Chlorination gives phosphonochloridates[408]

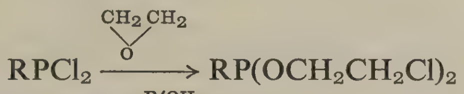


Dialkylphosphonous esters, in addition to preparation from phosphonous dichlorides, have been obtained (*a*) by the action of Grignard reagents on dialkyl and diaryl phosphorochloridites[409-10, 568] and trialkyl phosphites,[411] (*b*) by the reaction of the dichloride with alkylene oxides[412] to give 2-chloroalkyl esters, (*c*) by treatment of tetra-alkylphosphonous diamides with alcohols,[567, 1303] and (*d*) by transesterification of the lower alkyl ester with higher alcohols[399, 414]; no catalyst is required (cf. trialkyl phosphites). Higher alkyl dialkylphenyl phosphonates are conveniently obtained by transesterification of diphenylphenyl phosphonite and higher alcohols using diphenyl phosphite as catalyst.[2374] Cyclic esters:



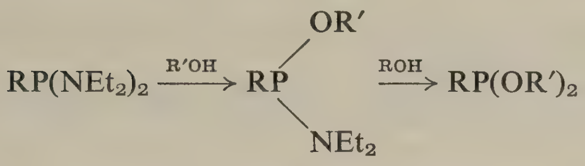
have been prepared by reaction of glycols with phosphonous dichlorides[1736] or with *N,N′*-tetra-alkylphosphonous diamides[1600]:

$$(R'O)_2PCl \xrightarrow{RMgX} (RO)_2P.R$$



$$RPCl_2 \xrightarrow{CH_2CH_2O} RP(OCH_2CH_2Cl)_2$$

$$RP(OMe)_2 \xrightarrow{R'OH} RP(OR')_2 + MeOH$$



$$RP(NEt_2)_2 \xrightarrow{R'OH} RP(OR')(NEt_2) \xrightarrow{ROH} RP(OR')_2$$

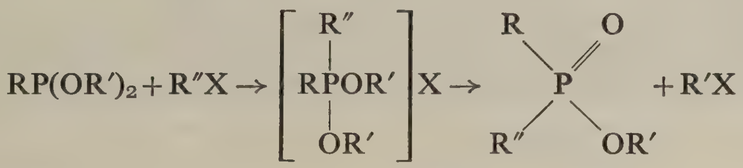
$$XMg(CH_2)_nMgX + 2(RO)_2PCl \rightarrow (RO)_2P(CH_2)_nP(OR)_2 \qquad (n = 4\text{–}6)^{568}$$

Phosphonous diesters undergo typical reactions of trivalent phosphorus compounds. They react readily with oxygen,[415] sulphur,[415–6] selenium,[416] and tellurium,[297] giving the corresponding phosphonate esters:

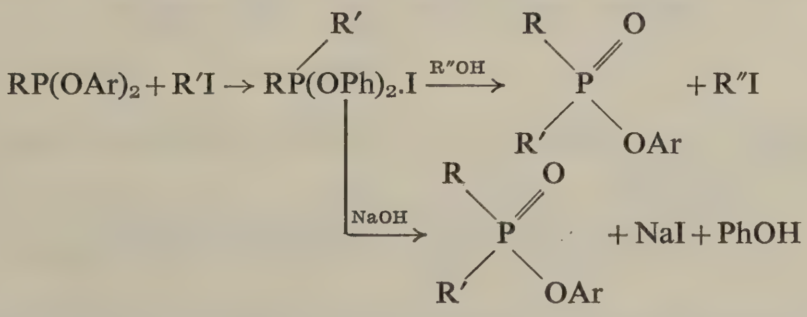
$$RP(OR')_2 \rightarrow RPX(OR')_2 \qquad (X = O, S, Se, Te)$$

Lower members such as diethyl methylphosphonite are reported to inflame on exposure to air on filter paper.[416] Many form crystalline complexes with cuprous halides ($RP(OR')_2,CuX$) which have sharp melting points and can be used for characterization.[415–6] They are hydrolyzed with one equivalent of water and a trace of acid to the mono-esters.[410]

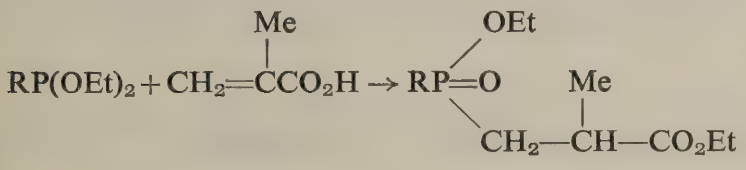
Like trialkyl phosphites the dialkyl phosphonites undergo the Arbuzov reaction with a wide variety of alkyl halides giving esters of phosphinic acids[415–8, 840]:



Reaction is usually complete in 2–3 hr. at 100°–120° compared with 5–6 hr. at 150°–160° required for trialkyl phosphites. Diaryl esters, like triaryl phosphites, do not undergo the Arbuzov rearrangement, but react with alkyl halides giving quasi-phosphonium compounds which may be decomposed by alcohols[421] (the Landauer–Rydon reaction) or by sodium hydroxide[422] giving phenyl esters of phosphinic acids:

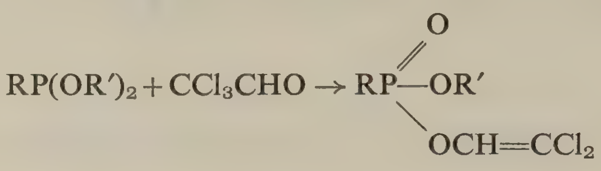


Dialkyl phosphonites react with α-β unsaturated acids such as acrylic or methacrylic acids giving phosphinic acid esters[1045, 1062]:



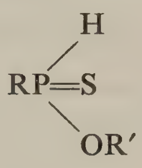
(R = Ph, Et)

α-Halogenoaldehydes react to give products which contain a new P–O bond rather than the expected P–C bond (the Perkow reaction[1010–11]—see p. 1011); thus, chloral gives a β,β-dichlorovinyl phosphonate[419]:

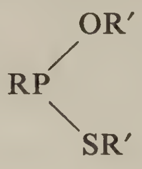


α-Halogenoketones may undergo the Arbuzov or Perkow reaction depending on the halogen and reaction conditions.[420]

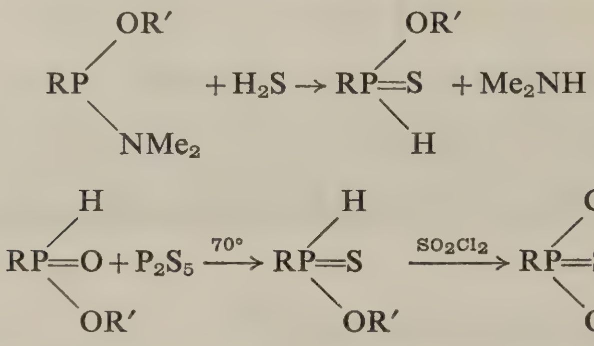
Phosphonochloridous esters react with hydrogen sulphide giving *O*-alkyl/aryl hydrogen phosphinothionates,[403]



and with mercaptans in the presence of tertiary organic bases giving *O*,*S*-dialkyl phosphonothioites[544]:



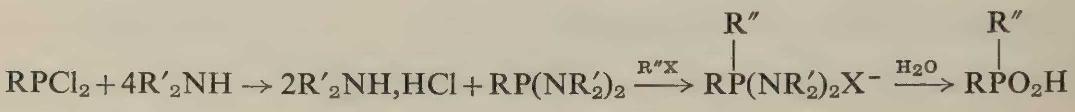
*O*-Alkyl hydrogen phosphinothionates are best prepared by the action of hydrogen sulphide on an *O*-alkyl-*N*,*N*-dimethyl phosphonamidite[569] or by the action of tetraphosphorus decasulphide on *O*-alkyl hydrogen phosphinates.[1735] They are readily chlorinated by sulphuryl chloride to *O*-alkyl phosphonochloridothionates[1735]:



The preparation and reactions of *S*,*S*-dialkyl phosphonodithioites have been described,[570, 945, 2375] e.g.,

$$RP(NMe_2)_2 + 2RSH \rightarrow RP(SR)_2 + 2Me_2NH$$
$$EtPCl_2 + 2RSH + 2Et_3N \rightarrow EtP(SR)_2 + 2Et_3NH,HCl$$

Phosphonous diamides are formed from the chlorides by reaction with secondary amines. Like the diesters they undergo reactions characteristic of tervalent phosphorus compounds and react with alkyl halides in an Arbuzov-type reaction to give quaternary salts which are readily hydrolyzed to phosphonic acids[446]:



$$RPCl_2 + 4R'_2NH \rightarrow 2R'_2NH,HCl + RP(NR'_2)_2 \xrightarrow{R''X} R\overset{R''}{\overset{|}{P}}(NR'_2)_2X^- \xrightarrow{H_2O} R\overset{R''}{\overset{|}{P}}O_2H$$

**Refs. p. 1082**

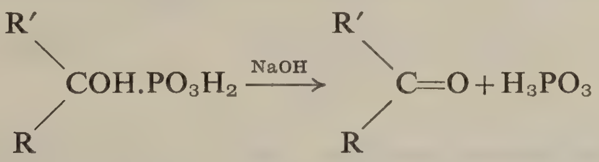
## Phosphonic Acids ($RPO_3H_2$) and their Esters

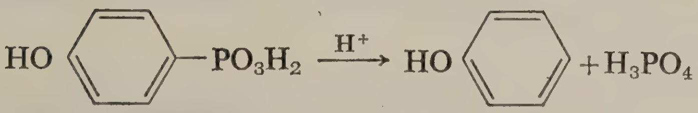
The preparation and properties of phosphonic acids have been reviewed by Kosolapoff,[1] and by Freedman and Doak.[456]

Phosphonic acids are generally crystalline compounds. They are dibasic acids. Dissociation constants of a considerable number of alkyl,[364, 458] halogenoalkyl,[364, 458] aryl,[457, 1274] vinyl,[571] triethylsilylalkyl[572] ($Et_3Si(CH_2)_nPO_3H_2$, $n = 1–4$), and alkylidine bis[742] phosphonic acids have been measured and the effects of structure and substituents discussed.[364, 456–8, 1269, 1274, 1306] Many of the dissociation constants are given by Kortüm, Vogel and Andrussow.[459] The effect of substituents on the dissociation constants is generally as would be expected; thus, electron-attracting substituents increase and electron-repelling substituents decrease the dissociation constant. The applicability of the Hammett equation to the dissociation constants of arylphosphonic acids[457] and of the Taft equation to the first and second dissociation constants of alkylphosphonic acids[1306] has been demonstrated. Molecular weight determinations on a number of phosphonic and phosphinic acids in acetic acid solution give normal molecular weights indicating absence of polymerization.[1308]

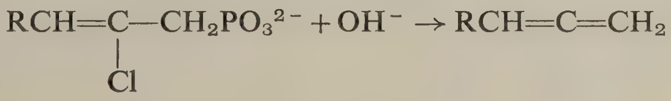
The carbon–phosphorus bond in these acids generally shows a high degree of stability and is unaffected by chemical reactions carried out on the organic residue. Thus, alkyl compounds having an $\alpha$-OH group may be dehydrated to $\alpha$-vinyl, or reduced by hydrogen iodide to $\alpha$-$CH_2$-compounds; those having $\alpha$-halogen may be dehydrohalogenated to give $\alpha$-vinyl groups, or the halogen can be replaced by reaction with amines or alkoxides; $\alpha$-vinyl groups add bromine and can be polymerized in the presence of radical initiators. Aromatic phosphonic acids undergo many reactions typical of aromatic compounds such as halogenation, nitration, reduction of nitro group to amino groups, and oxidation of alkyl groups to carboxyl.[2]

Although the P–C bond in phosphonic acids is generally very stable to hydrolytic fission (thus, phenylphosphonic acid is stable at 105° over 15 hours in 5–45% $H_2SO_4$[1305]), in a few classes of phosphonic acids, e.g., those having electron-attracting substituents attached to the $\alpha$-carbon atom, and *p*-hydroxyarylphosphonic acids,[1305] the P–C bond is readily cleaved by alkalis. Examples are trichloromethyl-, $\alpha$-hydroxyalkyl-, $\alpha$-cyanoalkyl-, and *p*-nitrobenzylphosphonic acids.[573] Aromatic phosphonic acids with hydroxyl or methoxyl groups attached to the nucleus in the *ortho*- or *para*-positions are cleaved in acid solution[471–2, 1305]:



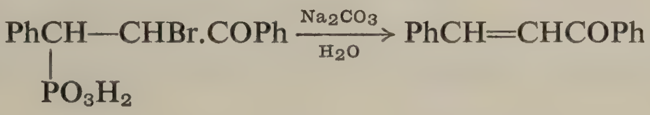


2-Chlorodecylphosphonic acid is reported to be decomposed almost instantly in water at pH 7 with the formation of dodecene. 2-Chloro-2-enylphosphonic acids are split by bases giving allenes[263]:



$$RCH{=}\underset{\displaystyle Cl}{\underset{|}{C}}{—}CH_2PO_3^{2-} + OH^- \rightarrow RCH{=}C{=}CH_2$$

$\beta$-Bromo-$\gamma$-keto acids are cleaved by alkalis giving olefins[453]:



$$\underset{\displaystyle PO_3H_2}{\underset{|}{PhCH}}{—}CHBr.COPh \xrightarrow[H_2O]{Na_2CO_3} PhCH{=}CHCOPh$$

Phosphonic acid analogues of ethylenediaminetetra-acetic acid and related compounds, e.g., ethylenediaminetetramethylenephosphonic acid $[(H_2O_3PCH_2)_2NCH_2]_2$, form relatively stable water soluble complexes with many metals.[517-8]

### PREPARATION OF PHOSPHONIC ACIDS

Phosphonic acids are obtained by hydrolysis of pentavalent compounds containing one P–C bond, such as tetrahalogenophosphoranes, phosphonyl halides, thionophosphine sulphides, and esters of phosphonic acids; and by oxidation of trivalent compounds such as $RPH_2$, $(RP)_4$, $RPO_2H_2$.

Esters are normally hydrolyzed by heating at reflux for several hours with concentrated hydrochloric acid. A mild hydrolysis route for unstable acids involves reaction with trimethylchlorosilane, the resulting trimethylsilyl ester being hydrolyzed by cold water[461]:

$$RPO(OR')_2 + Me_3SiCl \rightarrow 2R'Cl + RPO(OSiMe_3)_2 \xrightarrow{H_2O} RPO_3H_2$$

Benzyl groups may be removed from benzyl esters by hydrogenation with palladium catalyst.[460] Dialkyl alkylphosphonates eliminate olefin when heated at 250°–300°, giving the acid[462]:

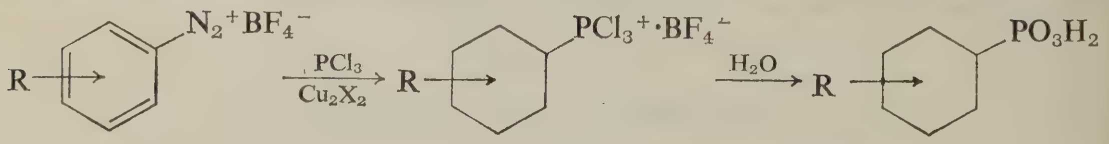
$$EtPO(OEt)_2 \xrightarrow{\Delta} EtPO_3H_2 + 2C_2H_4$$

The kinetics of hydrolysis of phosphonochloridates and phosphonate esters have been extensively studied by Hudson and co-workers.[474, 497-8, 1035] Silver ion exerts a considerable catalytic effect on the hydrolysis of dialkylphosphonothiolate esters.[484]

The more important methods for synthesis of phosphonic acids which involve P–C bond formation are outlined below.

#### *The Diazonium Fluoroborate Method*[463]

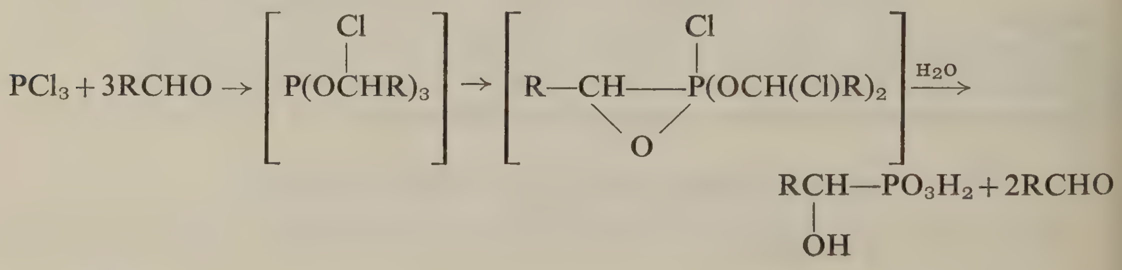
This is one of the most widely used methods for preparing aromatic phosphonic acids of known orientation. An aryldiazonium fluoroborate is caused to react with phosphorus trichloride in an inert solvent (ethyl acetate or dioxan) with cuprous bromide or chloride catalyst to give an aryltrichlorophosphonium fluoroborate which is hydrolyzed to phosphonic acid:



Aryldiazonium fluorosilicates have been used in place of the fluoroborate in a few cases.[464] Use of alkyl- or arylphosphonous dichloride in place of phosphorus trichloride gives a phosphinic acid.[475]

#### *The Reaction of Phosphorus Trihalides with Carbonyl Compounds*

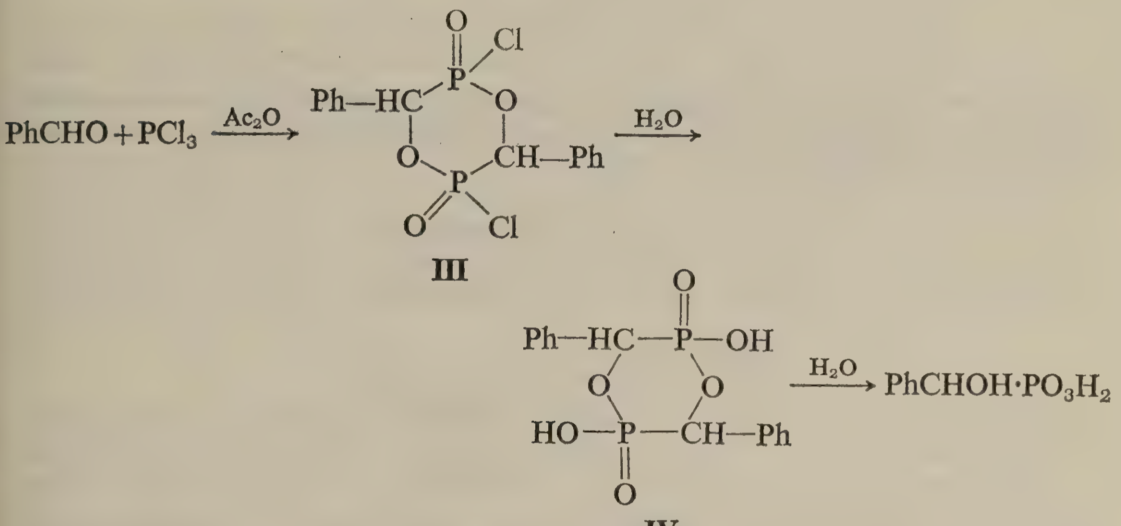
In addition to the high temperature reactions mentioned earlier phosphorus trichloride combines, at or near room temperature, with three moles of aldehyde[447] to form α-chloroesters of trivalent phosphorus which undergo the Arbuzov reaction.[378, 380] Hydrolysis yields 2 moles of aldehyde and one mole of α-hydroxyalkylphosphonic acid:



$$PCl_3 + 3RCHO \rightarrow \left[ P(O\overset{Cl}{\overset{|}{C}}HR)_3 \right] \rightarrow \left[ R{-}\underset{O}{\underbrace{CH{-}\overset{Cl}{\overset{|}{P}}}}(OCH(Cl)R)_2 \right] \xrightarrow{H_2O} \underset{\underset{OH}{|}}{RCH}{-}PO_3H_2 + 2RCHO$$

Physicochemical analysis of the system benzaldehyde–phosphorus trichloride proves the formation of a compound $PCl_3,3PhCHO$.[1326]

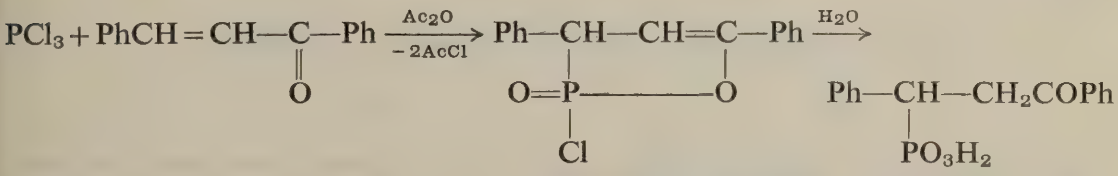
Addition of an aldehyde to an equivalent amount of phosphorus trichloride followed by hydrolysis with acetic acid[448] or acetic anhydride[449] gives acetyl chloride and a phosphonyl chloride which can be further hydrolyzed with water to α-hydroxyalkylphosphonic acid. Benzaldehyde and phosphorus trichloride[450] gave the cyclic phosphonyl chloride **III**, which by careful hydrolysis afforded the acid **IV**:



**III**

**IV**

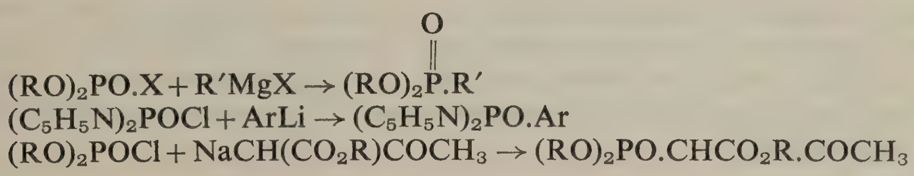
Other trivalent phosphorus halides, $PBr_3$, $ROPCl_2$, $(RO)_2PCl$, $RPCl_2$, $R_2PCl$ (but not $PI_3$) react like phosphorus trichloride with aldehydes[451, 453] giving respectively phosphonic acid, monoester of phosphonic acid, diester, phosphinic acid or *tert*-phosphine oxide. Unsaturated ketones, e.g., benzylidineacetophenone, react with phosphorus trichloride and acetic anhydride[451, 453-4] giving cyclic phosphonyl chlorides[449] which are hydrolyzed to γ-ketophosphonic acids:



Compounds of the type $APCl_2$ ($A = Ph$ or $OPh$)[451-3, 2370] react similarly to phosphorus trichloride.

### *Use of Organometallic Compounds*

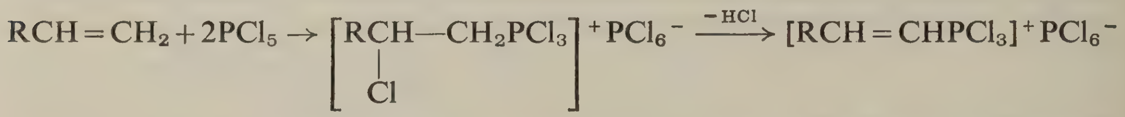
Grignard reagents react with dialkyl phosphorochloridates[465] or fluoridates,[521] and organolithium compounds with phosphoramidic chlorides[466] replacing the halogen atom and giving a carbon–phosphorus bond. Similarly, the sodium salts of aliphatic compounds containing active hydrogen such as ethyl acetoactate[467] react with phosphorochloridate. The products may be isolated as such or converted by hydrolysis to the acids:



$$(RO)_2PO.X + R'MgX \rightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}.R'$$
$$(C_5H_5N)_2POCl + ArLi \rightarrow (C_5H_5N)_2PO.Ar$$
$$(RO)_2POCl + NaCH(CO_2R)COCH_3 \rightarrow (RO)_2PO.CHCO_2R.COCH_3$$

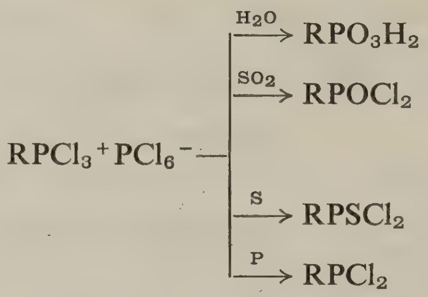
### *From Unsaturated Hydrocarbons and Phosphorus Pentachloride*

Phosphorus pentachloride adds readily to a wide variety of olefins having a terminal double bond to form crystalline complexes which are generally represented as 2-chloroalkyltrichlorophosphonium hexachlorophosphates. Many of these complexes readily lose hydrogen chloride giving the corresponding 1-alkenyl complexes[344-7, 1320]:



$$RCH{=}CH_2 + 2PCl_5 \rightarrow \left[\underset{\underset{Cl}{|}}{RCH}{-}CH_2PCl_3\right]^{+}PCl_6^{-} \xrightarrow{-HCl} [RCH{=}CHPCl_3]^{+}PCl_6^{-}$$

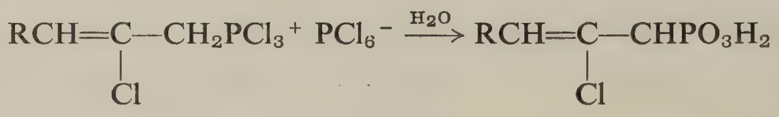
One report[348] claims that phosphorus pentachloride adds in the opposite sense to the olefin to form $RCH(PCl_3^{+})CH_2Cl.PCl_6^{-}$ as the initial product. Reactions of these complexes are indicated below:



Numerous workers (e.g., ref. 344) have claimed that 1-alkynes and phosphorus pentachloride interact to form β-chlorovinyl complexes of the type:

$$RCCl{=}CHPCl_3^{+}PCl_6^{-}$$

A recent investigation of the process shows that reaction of 1-alkynes with phosphorus pentachloride is accompanied by a hydride shift to form 2-chloroalkyl-2-enylphosphonium complexes which, by hydrolysis, yield 2-chloro-2-enylphosphonic acids[263]:



$$RCH{=}\underset{\underset{Cl}{|}}{C}{-}CH_2PCl_3^{+}\ PCl_6^{-} \xrightarrow{H_2O} RCH{=}\underset{\underset{Cl}{|}}{C}{-}CHPO_3H_2$$

Reactions of phosphorus pentachloride with conjugated dienes such as butadiene[349, 1350] and vinylacetylene[1317] are reported. The precise structures of the complexes so formed and of the phosphonic acids derived from them have yet to be established with certainty. However, 1-phenylbutadiene with phosphorus pentachloride or phenyl tetrachlorophosphorane is reported to form compounds **I** and **II** respectively as indicated below.[2371] The adduct from piperylene and phosphorus pentachloride yields penta-1:3-dienyl phosphonyl dichloride after treatment with sulphur dioxide.[2372]

$$\underset{\textbf{I}}{(PhCH{=}CH{-}CH{=}CH)_2PCl_3} \qquad \underset{\textbf{II}}{PhCH{=}CH{-}CH{=}CH{-}P(Ph)Cl_3}$$

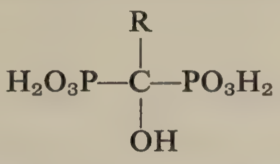
### *Miscellaneous Methods*

The direct phosphonylation of benzene with phosphoric acid has not been reported. Hexagonal phosphorus pentoxide reacts with benzene at 250°–325°C. to give a product $ArHP_4O_{10}$ which by hydrolysis yields phenylphosphonic acid. Yields are poor except when a large excess of benzene is used.[468] A few other aromatic hydrocarbons react similarly.

Phosphorous acid adds to olefins in the presence of free-radical catalysis[469, 470]:

$$\mathrm{RCH{=}CH_2 + H_3PO_3 \rightarrow RCH_2CH_2PO_3H_2}$$

Compounds claimed to be alkylhydroxymethylene bisphosphonates,



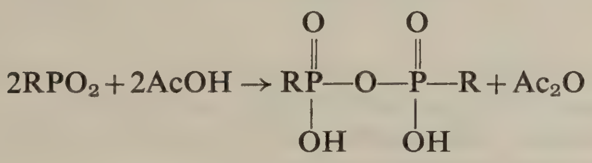
$$\mathrm{H_2O_3P{-}\underset{\displaystyle OH}{\overset{\displaystyle R}{C}}{-}PO_3H_2}$$

are obtained from phosphorous acid and carboxylic acid anhydrides[481] or from organic acids, water and phosphorus trichloride.[482] 'Acetyl phosphite', formed by interaction of phosphorous acid and acetic anhydride, has been shown to consist largely of monoacetyl phosphonate, $\mathrm{CH_3COPO_3H_2}$.[584] Nitrilotrismethylenephosphonic acid, $\mathrm{N(CH_2PO_3H_2)_3}$, is formed in high yield by the interaction of ammonium chloride, formaldehyde, and phosphorous acid.[1311] Addition of phosphorous acid to dialkyl maleates gives esters of phosphonosuccinic acid.[1324]

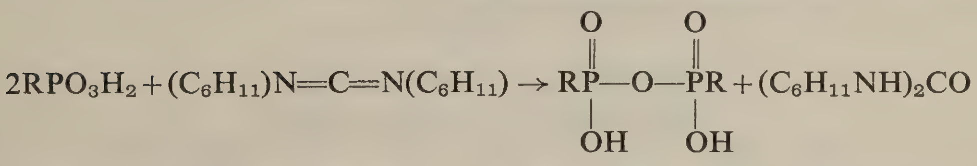
Tetraphenyl silicate and phosphorus pentasulphide interact at 195° to give, after hydrolysis of the intermediate product, a 41% yield of *p*-hydroxyphenylphosphonic acid.[523]

### Anhydrides of Phosphonic Acids

Polymeric anhydrides of the type $\mathrm{(RPO_2)}_n$ are formed by the interaction of phosphonyl dihalides and phosphonic diesters[1, 1318–9, 2379] and by treating a phosphonic dichloride with formic acid[1677, 2377] or with one mole of water at 120°–130° under vacuum.[2056, 2378] Van Wazer and co-workers have examined the NMR spectra of the polymeric methyl and phenyl phosphonic anhydrides formed by several of the above methods. They consider the compounds as condensation polymers which, depending on the proportions of reagents used and polymerization conditions, consist of mixtures of chain molecules of the type $\mathrm{X{-}PO.R[OPO.R]}_n\mathrm{X}$ (where $\mathrm{R=CH_3}$, $\mathrm{X=OCH_3}$, Cl, OH; where R = Ph, X = Cl, OH).[2379] Pyrophosphonic acids have been obtained[476] by the action of di*cyclo*hexyl carbodi-imide (DCC) on the acids, and by the action of acetic acid on phosphonic anhydrides[2380]:

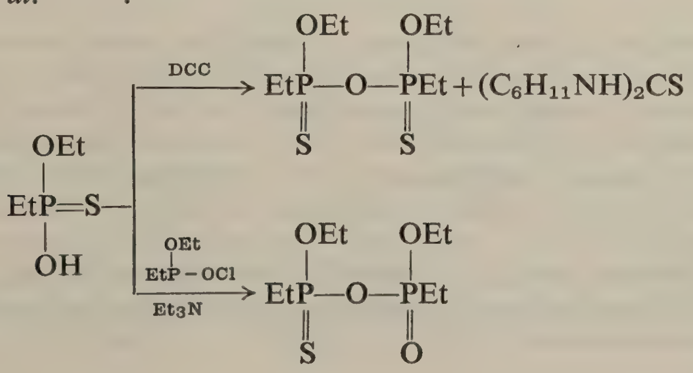


$$\mathrm{2RPO_2 + 2AcOH \rightarrow R\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}O{-}\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}R + Ac_2O}$$



$$\mathrm{2RPO_3H_2 + (C_6H_{11})N{=}C{=}N(C_6H_{11}) \rightarrow R\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}O{-}\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}R + (C_6H_{11}NH)_2CO}$$

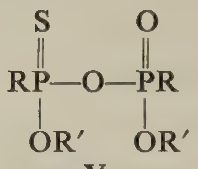
Dialkyl pyrophosphonates are readily obtained from monoalkyl phosphonates[476] using DCC. The stereochemistry of the reactions of ethyl ethylphosphonothioic acid to diethyl *PP′*-diethyl dithiopyrophosphonate with DCC and to diethyl *PP′*-diethyl thiopyrophosphate with ethyl ethylphosphonochloridothionate has been examined by Michalski *et al.*[2381–2]:



$$\mathrm{Et\underset{\displaystyle OH}{\overset{\displaystyle OEt}{P}}{=}S \xrightarrow{DCC} Et\underset{\displaystyle S}{\overset{\displaystyle OEt}{P}}{-}O{-}\underset{\displaystyle S}{\overset{\displaystyle OEt}{P}}Et + (C_6H_{11}NH)_2CS}$$

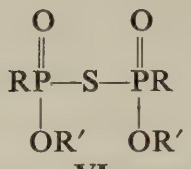
$$\mathrm{Et\underset{\displaystyle OH}{\overset{\displaystyle OEt}{P}}{=}S \xrightarrow[Et_3N]{Et\overset{OEt}{P}-OCl} Et\underset{\displaystyle S}{\overset{\displaystyle OEt}{P}}{-}O{-}\underset{\displaystyle O}{\overset{\displaystyle OEt}{P}}Et}$$

The infra-red spectrum of dialkyl monothiopyrophosphonates indicates the thiono structure V, as for analogous tetra-alkyl thiopyrophosphates, rather than the thiolo structure VI[354]:



$$\underset{OR'}{\overset{S}{\overset{\|}{RP}}}-O-\underset{OR'}{\overset{O}{\overset{\|}{PR}}}$$

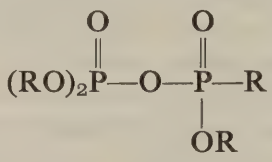
V



$$\underset{OR'}{\overset{O}{\overset{\|}{RP}}}-S-\underset{OR'}{\overset{O}{\overset{\|}{PR}}}$$

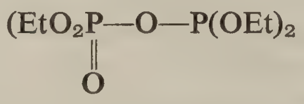
VI

Esters of isohypophosphonic acid:



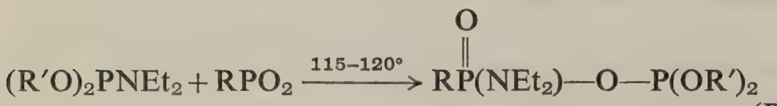
$$(RO)_2\overset{O}{\overset{\|}{P}}-O-\underset{OR}{\overset{O}{\overset{\|}{P}}}-R$$

are formed by heating $(RO)_2POCl$ with $(RO)_3P$ or $RPO(OR)_2$ ($R = Me, Et$),[1451] or by an Arbuzov reaction between tetraethyl *iso*hypophosphate:



$$(EtO_2\underset{O}{\underset{\|}{P}}-O-P(OEt)_2$$

and ethyl iodide.[1584] Amide anhydrides of mixed $P^{III}P^{V}$ acids are formed by the interaction of phosphorous amides and phosphonic anhydrides[2419]:



$$(R'O)_2PNEt_2 + RPO_2 \xrightarrow{115\text{–}120°} R\overset{O}{\overset{\|}{P}}(NEt_2)-O-P(OR')_2$$

($R = Me, Ph; R' = Pr, Bu$)

Dimeric arylthionophosphine sulphides result from the reaction of benzene or aromatic hydrocarbons with tetraphosphorus decasulphide at elevated temperature.[338,480] If the reaction is conducted in the presence of aluminium trichloride, benzene gives diphenylphosphinodithioic acid[328]:

$$ArH + P_4S_{10} \rightarrow (ArPS_2)_2 + P_4S_7$$

$$C_6H_6 + P_4S_{10} \xrightarrow{AlCl_3} (C_6H_5)_2PS_2H$$

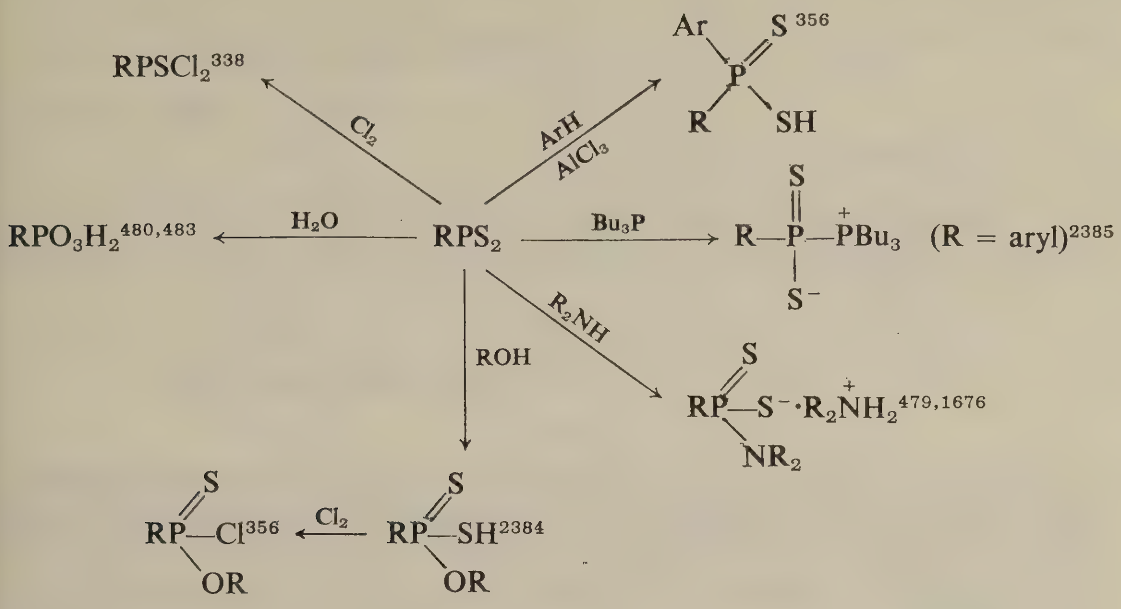
Alkyl and aryl thionophosphine sulphides result from the action of hydrogen sulphide on phosphonothionic dichlorides[356,2366]:

$$RPSCl_2 + H_2S \rightarrow (RPS_2)_2 + 2HCl$$

Many olefins react with tetraphosphorus decasulphide giving products of unknown structure which have found wide commercial use as oil additives.[3] *cyclo*Hexene gives dimeric *cyclo*hexenyl thionophosphine sulphide,[483] which is converted by hydrolysis to $\Delta^2$-*cyclo*hexenephosphonic acid. With a 25% excess of tetraphosphorus decasulphide, hexene-2, octene-2 and decene-2 form dithiophosphinic acids $R_2PS_2H$ in which the carbon–carbon double bonds are preserved; an allylic type addition has been postulated.[2383]

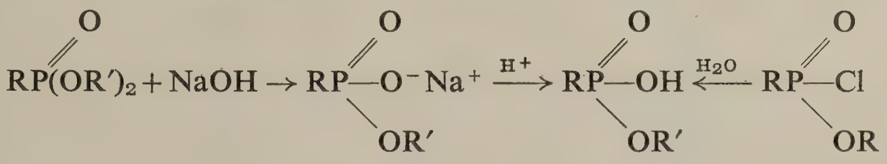
An *X*-ray diffraction analysis of methylthionophosphine sulphide shows it to be dimeric.[478,1675] Cryoscopic measurements on the phenyl compound (from $PhPH_2$ and $S_2Cl_2$) indicate a trimer.[479]

The thionophosphine sulphides are interesting intermediates. Some of their reactions are indicated below:

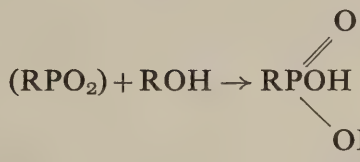


## Monoesters of Phosphonic Acids

Monoalkyl esters of alkyl- and arylphosphonic acids are readily obtained from the diesters by refluxing with aqueous or alcoholic sodium hydroxide,[473] by the action of alcohols on phosphonic acid anhydrides[1318-9, 1677, 2056, 2377] or by single dealkylation of the diesters by heating with alkali metal halides[1322]:



$$RP(OR')_2 + NaOH \rightarrow R\overset{O}{\underset{OR'}{P}}—O^-Na^+ \xrightarrow{H^+} R\overset{O}{\underset{OR'}{P}}—OH \xleftarrow{H_2O} R\overset{O}{\underset{OR}{P}}—Cl$$

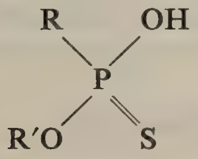


$$(RPO_2) + ROH \rightarrow R\overset{O}{\underset{OR}{P}}OH$$

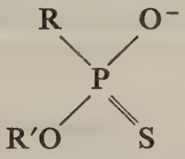
$$RPO(OR)_2 + MX \rightarrow RPO.OMOR + RX \qquad (X = Br, I)$$

Dissociation constants of several monoalkyl phosphonates are reported.[485, 571]

Kabachnik *et al.* concluded from physical evidence that *O*-alkylphosphonothioic acids[486] and their salts[487] exist largely in the forms **VII** and **VIII** indicated below:

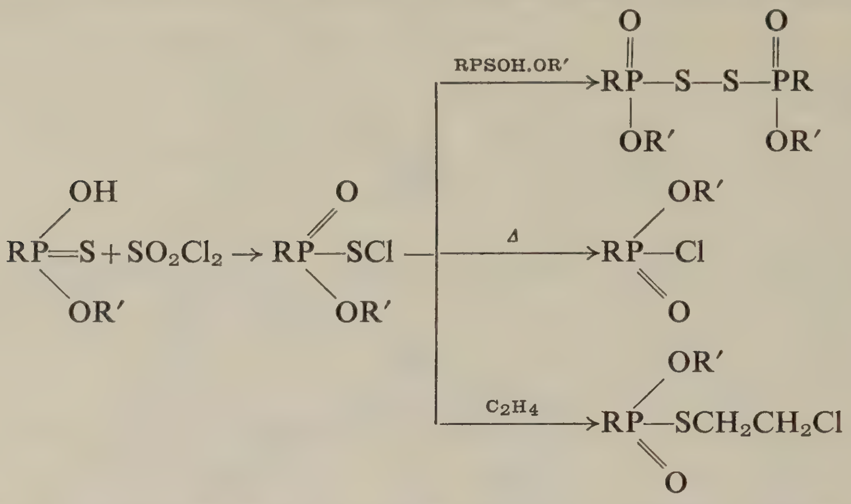


**VII**

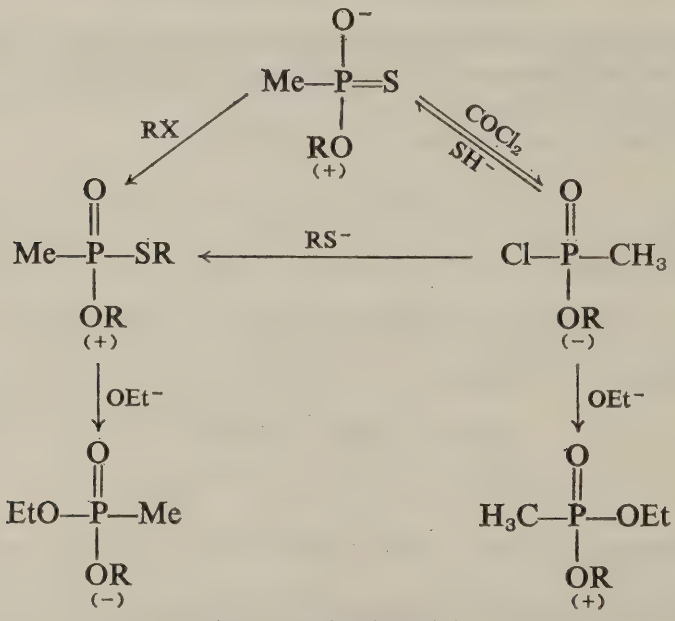


**VIII**

The salts react with alkyl halides giving *S*-alkyl esters, but with acyl halides giving *O*-acyl anhydrides.[487] Chlorination of *O*-alkylalkylphosphonothioic acids with sulphuryl chloride gives either *P*-alkoxy-*P*-alkyloxophosphoranesulphenyl chlorides or bis(*P*-alkoxy-alkylphosphinyl) disulphides depending on the amount of reagent used.[404, 489] The sulphenyl chlorides are thermally unstable and decompose to alkylalkylphosphonochloridates. They add to olefins giving $\beta$-chloroethyl esters:



Asymmetric phosphonic acid derivatives such as *O*-phenyl-*N*-($\beta$-dimethylaminoethyl)-*P*-phenylphosphonamidate[490] and a number of *O*-alkylphosphonothioic acids[491-2] have been resolved into optical isomers. The optically active acids have proved a particularly valuable starting point for the study of the stereochemistry of displacement reactions at the phosphorus atom. A sequence of reactions established by Aaron and his co-workers is shown below[493]:



$(R = -CH(CH_3)_2)$

Optically active dialkyl monothioalkylpyrophosphonates, prepared from optically active *O*-alkyl alkylphosphonothionic acid and the *O*-alkyl alkylphosphonochloridate, have been used to follow the stereochemical course of pyrophosphate hydrolysis.[495-6]

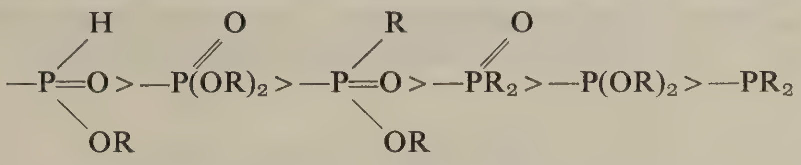
### Diesters of Phosphonic Acids

Vapour pressures,[1396, 1430] densities,[1430] dipole moments[1414] and viscosities[948] of a number of alkyl phosphonates are recorded.

These esters (e.g., dioctyl phenylphosphonate) are thermally more stable than the corresponding trialkyl phosphates (e.g., trioctyl phosphate).[499] As in phosphonic acids the C–P bond generally exhibits a high degree of stability. The diesters undergo numerous reactions[2] in which the P–C and P–OC bonds remain intact. For example, hydroxyl groups in alkyl phosphonates may be replaced by amino groups by ammonolysis, and aminoalkyl compounds react with phosgene to give isocyanates which undergo the typical reactions of organic isocyanates.[501] In vinyl phosphonates the phosphoryl group activates the double bond for addition of nucleophilic reagents and for the Diels–Alder reaction with conjugated dienes[519, 520, 580]:

$$XH + H_2C{=}CH{-}PO(OR)_2 \xrightarrow{\text{base}} XCH_2CH_2PO(OR)_2$$
$$(X = CH(CO_2R)_2,\ RS,\ R_2N,\ (RO)_2PO,\ RO)$$

Kabachnik *et al.* showed that secondary amines add to the $\beta$-position of the vinyl group of vinyl phosphorus compounds regardless of the valency of the phosphorus atom or the groups attached to it. The reactivity decreased in the following order[578]:



$$-P(H)(OR){=}O > -P(O)(OR)_2 > -P(R)(OR){=}O > -P(O)R_2 > -P(OR)_2 > -PR_2$$

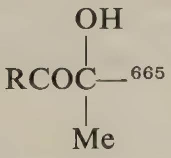
1-Alkynyl phosphonates can undergo additions of nucleophiles to the acetylenic bond.[521] In electrophilic substitutions of aryl phosphonates the phosphonyl group is largely *meta*-directing.[522] Polar substituent constants for the groupings

$$-CH_2PO(OR)_2, \qquad -CH_2POR_2, \qquad -CH_2PSR_2 \qquad -CH_2\overset{+}{P}R_3$$

have been determined.[2386]

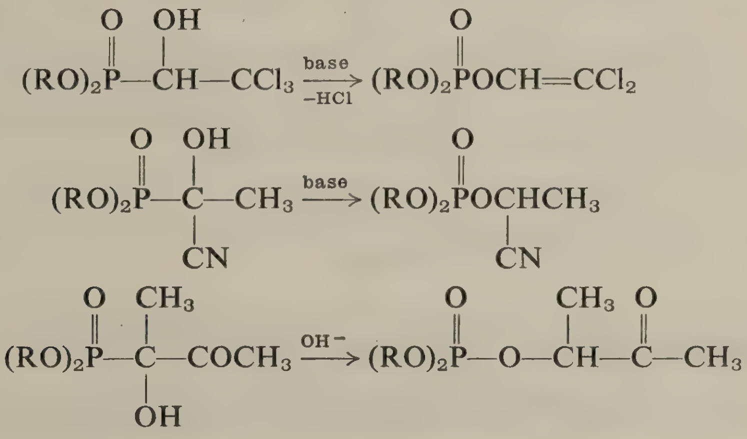
Ester groups of phosphonic esters undergo transesterification; allyl esters polymerize in the presence of radical initiators[499, 502] and can be co-polymerized with compounds such as styrene, methyl methacrylate, vinyl acetate and allylcarboxylic acid esters. Glassy solids having considerable flame-resistance are obtained when the substituent attached to phosphorus is more electronegative than methyl (e.g., diallyl phenylphosphonate) whereas when the substituent is methyl or a group with electronegativity similar to, or more positive than, methyl the polymers range from soft solids to rubbery gels.[502]

Some exceptions to the general stability are compounds which have electronegative substituents attached to the $\alpha$-carbon atom. In compounds with $CF_3$—, $CCl_3$—,[504] or RCHOH–[503] groups attached to phosphorus the P–C bond is readily cleaved by alkalis. $\alpha$-Keto esters are cleaved by acid[505]; aroylphosphonic esters are cleaved by dilute acid or base.[500] Compounds with $CH_3C(CN)OH$–,[508-9] $CCl_3CHOH$–[506, 908, 1007, 1014, 1036, 1192] or



$$RCOC(OH)(Me){-}^{665}$$

groups undergo rearrangement on treatment with alkali giving phosphoric acid derivatives:

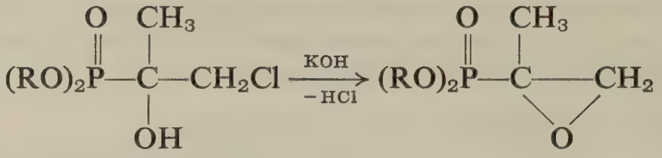


$$(RO)_2P(O){-}CH(OH){-}CCl_3 \xrightarrow[-HCl]{\text{base}} (RO)_2P(O)OCH{=}CCl_2$$

$$(RO)_2P(O){-}C(OH)(CN){-}CH_3 \xrightarrow{\text{base}} (RO)_2P(O)OCH(CN)CH_3$$

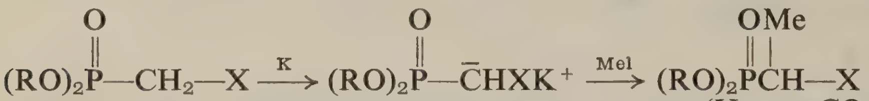
$$(RO)_2P(O){-}C(CH_3)(OH){-}COCH_3 \xrightarrow{OH^-} (RO)_2P(O){-}O{-}CH(CH_3){-}C(O){-}CH_3$$

A number of dialkyl 2-chloro-1-hydroxy-1-methylethylphosphonates eliminate hydrogen chloride on treatment with alkali giving 1,2-epoxyalkylphosphonates[1037-8]:



Diethyl 2-pyrrylphosphonate undergoes facile P–C bond cleavage on treatment with aqueous sodium hydroxide to give a mixture of pyrrole and 2-ethylpyrrole.[1986]

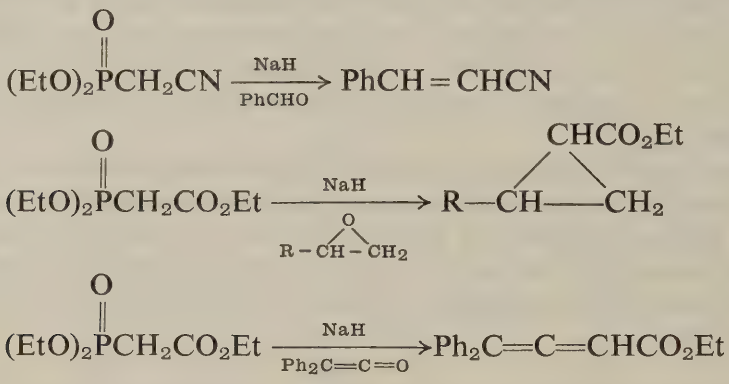
The α-hydrogen atom of phosphonates, particularly those with electronegative substituents attached to the α-carbon atom, is replaceable by metals giving phosphonate anion salts which can be alkylated with alkyl halides. Tetra-alkyl methylenediphosphonate[511] and trialkylphosphonacetic acid[510] react in this way:



$$(RO)_2\overset{O}{\overset{\|}{P}}-CH_2-X \xrightarrow{K} (RO)_2\overset{O}{\overset{\|}{P}}-\bar{C}HXK^+ \xrightarrow{MeI} (RO)_2\overset{O\ Me}{\overset{\|\ \ |}{PCH}}-X$$

$(X = -CO_2Et \text{ or } -PO.(OR)_2)$

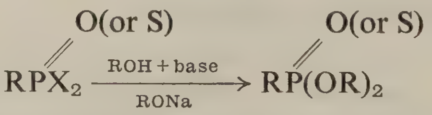
The preparation and characterization of a number of salts NaL, $ZnL_2$, $CrL_3$ (where L = the phosphonate anion $(EtO)_2PO.CH\text{–}COCH_3{}^-$) are reported.[1489] Wadsworth and Emmons[512] have extended the use of phosphonate anions to olefin synthesis using sodium hydride for their generation. Reaction of the anion with aldehydes or ketones, epoxides and ketenes yields olefins, *cyclo*propanes and allenes respectively. Olefins formed by this method generally have a *trans*-configuration about the C=C double bond.[441] The reaction between optically active styrene oxide and phosphonate carbanions proceeds with inversion of configuration at the asymmetric centre[1306, 1312]:



Further work on olefin preparations by this method is described.[1513-6]

### PREPARATION

The direct esterification of phosphonic acids with alcohols has not been reported. Alkyl esters may be obtained from the phosphonyl dihalide by treatment with an excess of the alcohol in the cold under reduced pressure to remove hydrogen chloride,[309] or more generally by use of alcohol and tertiary base or sodium alkoxide. Boron trifluoride catalyzes the reaction of phosphonodichloridothionates with alcohols.[524] Aryl esters are not dealkylated by hydrogen chloride and can be prepared by heating the phosphonyl dihalide and phenol:



Transesterification, although slow, may be used to prepare mixed and higher esters of alkane phosphonic acid[414, 715] (see also p. 1033).

$$MePO.(OEt)_2 + ROH \xrightarrow{\text{base}} MePO.OEtOR + EtOH \xrightarrow{ROH} MePO(OR)_2 + EtOH$$

Asymmetric esters of alkyl and aryl phosphonic acids may be obtained by treating a tetramethylammonium methylphosphonate with alkyl halides[2378]:

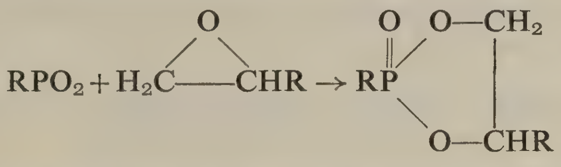
$$\mathrm{RPO(OMe)_2 + Me_3N \rightarrow RP(O)(OMe)O^- Me_4N^+ \xrightarrow{RX} RP(O)(OMe)OR + Me_4NX}$$

Numerous alkyl- and substituted alkylphosphonic acids have been prepared by reactions which start with dialkyl hydrogen phosphonates or trialkyl phosphites (pages 988, 989, 991, 994, 1006).

Vinyl esters, $\mathrm{RPO(OCH{=}CH_2)_2}$, are formed in the reaction of the corresponding chlorides with acetaldehyde and tertiary amine[1506]:

$$\mathrm{RPOCl_2 + CH_3CHO \xrightarrow{Et_3N} RPO(OCH{=}CH_2)_2} \qquad (\mathrm{R} = \text{alkyl, vinyl, aryl})$$

Cyclic esters of alkylphosphonic acids have been obtained by the action of oxiranes on phosphonic acid anhydrides[2056]:



Dialkylselenophosphonic acid can be readily obtained by refluxing an equimolar mixture of alkylphosphonous dichloride, alcohol and selenium in benzene solution. Similar preparation of the tellurium analogues failed, owing to their instability.[2058]

Photolysis of iodobenzene in the presence of trialkyl phosphite affords a mixture of dialkyl phenylphosphonate and alkyl iodide. The only competing reaction is the Arbuzov reaction between the phosphite and by-product alkyl iodide. An excess of phosphite and low temperature favour high yields. In a similar reaction triphenylphosphine and triphenyl phosphite give phosphonium salts[2006, 2415]:

$$\mathrm{PhI + (RO)_3P \xrightarrow{u.v.} PhPO(OR)_2 + RI}$$
$$\mathrm{PhI + (PhO)_3P \xrightarrow{u.v.} PhP(OPh)_3{}^+I^-}$$
$$\mathrm{PhI + Ph_3P \xrightarrow{u.v.} Ph_4\overset{+}{P}I^-}$$

Photolysis of 5-valent phosphorus compounds having a P–H bond and chlorine in an excess of *cyclo*hexane gives 75–85% yields of compounds with a *P–cyclo*hexyl bond. Dialkyl *cyclo*hexyl phosphonates are formed from dialkyl phosphites, alkyl phosphonite affords a phosphinic ester and secondary phosphine oxide a tertiary phosphine oxide. Similar radical reactions take place using compounds having a P–Cl bond and are catalyzed by radiation below 220 mμ[2416]:

$$\mathrm{(RO)_2P(O)H + C_6H_{12} + Cl_2 \xrightarrow{u.v.} C_6H_{11}PO(OR)_2}$$
$$\mathrm{RO(R)P(O)H + C_6H_{12} + Cl_2 \xrightarrow{u.v.} C_6H_{11}(R)P(O)OR}$$
$$\mathrm{Et_2P(O)Cl + C_6H_{12} \xrightarrow{u.v.} Et_2P(O)C_6H_{11}}$$

### **Phosphinous Acids** (see Secondary Phosphine Oxides)

#### ESTERS OF PHOSPHINOUS ACIDS, $\mathrm{R_2P{-}OR}$

Phosphinite and phosphinothioite esters have been prepared by the action of alcohols or mercaptans on phosphinyl halides in the presence of tertiary organic bases[329, 526, 1919, 2387] and by the action of alcohols on *N,N*-dimethyl phosphinous amides[413, 576]:

$$\mathrm{R_2PCl + R'OH \xrightarrow{R_3N} R_2POR' + R_3N,HCl}$$
$$\mathrm{R_2PCl + R'SH \xrightarrow{R_3N} R_2PSR' + R_3N,HCl}$$
$$\mathrm{R_2P{-}NMe_2 + R'OH \rightarrow R_2P{-}OR' + Me_2NH}$$

Grignard reagents react with phosphorodichloridites[411, 494] or with *O*-alkyl phosphonochloridites[544] giving the phosphinite ester. The use of powdered Grignard reagent in non-ethereal solvents gives good yields[525]:

$$RO{-}PCl_2 + 2R'MgX \rightarrow R'_2P{-}OR$$

*N,N*-Dimethyl phosphinous amides may be synthesized from aryl-lithium compounds and *N,N*-dimethyl-*O*-alkylphosphorochloridite[576] from the phosphinous halides and dimethylamine or by alkylation of *N,N*-dimethyl phosphoroamidodichloridite with organo-aluminium[477] compounds. They exchange with phosphorus trichloride to form phosphinous chloride[477]:

$$3Me_2NPCl_2 + 2AlR_3 \rightarrow 3Me_2NPR_2 + 2AlCl_3$$
$$Et_2NPEt_2 + PCl_3 \rightarrow Et_2NPCl_2 + Et_2PCl$$

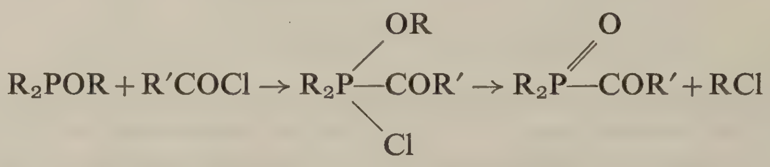
Acyl bis(trifluoromethyl)phosphinates have been recently described; they are prepared by the reactions[1597]:

$$(CF_3)_2PX + AgOAc \rightarrow (CF_3)_2POCOCH_3 \qquad (X = Cl, Br)$$
$$[(CF_3)_2P]_2O + (CH_3CO)_2O \rightarrow (CF_3)_2POCOCH_3$$

The phosphinite esters readily undergo typical reactions of trivalent phosphorus compounds, forming complexes with heavy metal halides such as cuprous halides[1919] and adding sulphur to give phosphinothioic esters.[526] They readily isomerize on heating giving tertiary phosphine oxides. The order of reactivity of trivalent phosphorus compounds with alkyl halides increases in the series[527]:

$$(RO)_3P < RP(OR')_2 < R_2POR' < R_3P$$

Reaction of phosphinites with alkyl halides such as methyl iodide, or acyl halides, in the Arbuzov reaction is spontaneous and exothermic.[526, 1919] Several examples of isolable onium intermediates are reported[2387, 2388]:



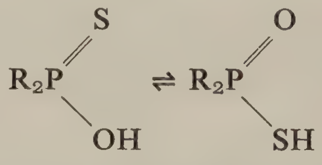
$$R_2POR + R'COCl \rightarrow R_2\overset{OR}{\underset{Cl}{P}}{-}COR' \rightarrow R_2\overset{O}{\overset{\|}{P}}{-}COR' + RCl$$

Alkyl diphenylphosphonites undergo the expected Perkow reaction with chloral to form *β,β*-dichlorovinyl diphenylphosphinate.[494] In common with esters of phosphorous and phosphonous acids, the phosphinous lower esters readily undergo transesterification[577]:

$$R_2POEt + R'OH \rightarrow R_2POR' + EtOH$$

## Phosphinic Acids, $R_2PO_2H$

These are monobasic acids which are generally crystalline. Dissociation constants of several symmetrical dialkylphosphinic acids are given by Crofts and Kosolapoff[364] and by Kabachnik *et al.*[1269, 1274] The position of the equilibrium,



$$R_2\overset{S}{\overset{\|}{P}}{-}OH \rightleftharpoons R_2\overset{O}{\overset{\|}{P}}{-}SH$$

in monothiophosphinic acids has been determined from p$K$ measurements on the acids[1269] (see Table VII, p. 1036). Acid strengths of diethylphosphinic acids increase on replacing the oxygen atoms successively by sulphur and selenium (cf. ref. 2389).

The diseleno acid is stable for only a short time in aqueous solution; salts such as $Et_2P(Se)SeNa,2H_2O$ can be isolated.

p*K* in 80% aqueous *iso*propyl alcohol

| $Et_2PO_2H$ | $Et_2P(S)OH$ | $Et_2P(S)SH$ | $Et_2P(S)SeH$ | $Et_2P(Se)SeH$ |
|---|---|---|---|---|
| | 4·98 | 2·6 | 2·29 | 2·18 |

The vapour pressures of liquid $Me_2PO_2H$, b.p. 377° at 760 mm. Hg, are recorded.[1388] The C–P bond in these compounds, like that in phosphonic acids, is very stable; exceptions are compounds having α-hydroxy, α-keto, trichloromethyl or trifluoromethyl groups attached to the phosphorus atom.

PREPARATION

Common methods of preparation are by hydrolysis of phosphinyl halides and hydrolysis of phosphinic esters:

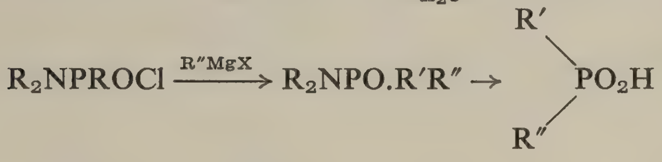
$$R_2POCl \xrightarrow{H_2O} R_2PO_2H$$
$$R_2PSCl \xrightarrow{H_2O} R_2PS.OH^{430}$$
$$R_2PSCl \xrightarrow{NaSH} R_2PS_2H^{429}$$
$$R_2POOR \xrightarrow{HCl} R_2PO_2H$$

A number of the more important methods of synthesizing phosphinic acids have been mentioned earlier. These are, hydrolysis of Kinnear–Perren complexes and diaryldichlorophosphonium tetrafluoroborates, the fission of tertiary phosphine oxides with sodium hydroxide, and the reaction of phosphorus pentasulphide, aluminium trichloride aromatic and hydrocarbons, giving dithio acids. Other methods are:

*From Grignard Reactions*

Grignard reagents react with phosphorus oxychloride replacing the chlorine atoms in a stepwise manner giving tertiary phosphine oxides as final products. By reverse addition two chlorine atoms may be replaced giving, after hydrolysis, the phosphinic acid.[431–2] A better method involves replacement of one chlorine atom in phosphoryl chloride[433] or a phosphonyl dichloride[382, 435] with a dialkylamine giving *N,N*-dialkyl phosphoramidic dichloride and *N,N*-dialkyl phosphonamidic chloride respectively, followed by reaction with Grignard reagent:

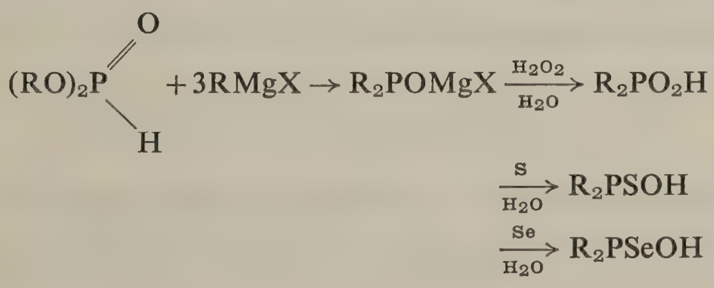
$$POCl_3 + 2RMgX \rightarrow R_2POCl.2MgXCl \xrightarrow{H_2O} R_2PO_2H$$
$$R_2NPOCl_2 \xrightarrow{2R'MgX} R_2NPOR'_2 \xrightarrow[H_2O]{H^+} R'_2PO_2H$$



$$R_2NPROCl \xrightarrow{R''MgX} R_2NPO.R'R'' \rightarrow R'R''PO_2H$$

*Miscellaneous Methods*

Grignard reagents react with dialkyl hydrogen phosphonates giving secondary phosphine oxides which may be oxidized with hydrogen peroxide to the phosphinic acid.[364] Phosphinothioic and phosphinoselenoic acids have been obtained by adding sulphur[430] or selenium[428] to the intermediate magnesium halide salt of the phosphine oxide:



$$(RO)_2P(O)H + 3RMgX \rightarrow R_2POMgX \xrightarrow[H_2O]{H_2O_2} R_2PO_2H$$
$$\xrightarrow[H_2O]{S} R_2PSOH$$
$$\xrightarrow[H_2O]{Se} R_2PSeOH$$

Tetrasubstituted diphosphine disulphides are an important starting point for the synthesis of symmetrical and unsymmetrical phosphinic acids. They are readily oxidized to phosphinic acids,[426, 1903] and by treatment with elemental sulphur and ammonium hydroxide[585] or with sulphur and sodium sulphide[586] yield ammonium or sodium salts of the corresponding phosphinodithioic acids. Phosphorus pentasulphide and methyl magnesium bromide give a small yield of dimethyl phosphinodithionate (isolated as the nickel salt).[134] The dithio acids are readily oxidized by iodine to bis(thiophosphinyl) disulphides.[586] Heavy metal salts of phosphinodithioic acids have been described.[2390]

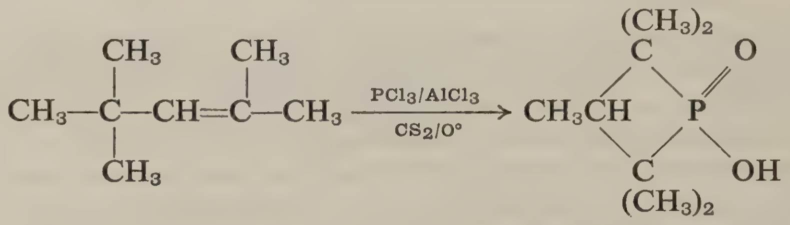
Tertiary aromatic amines such as *N,N*-dimethylaniline react with phosphoryl chloride replacing the chlorine atoms successively with *p*-dialkylaminophenyl groups. Use of two equivalents of dimethylaniline gives, after hydrolysis, bis(*p*-dimethylaminophenyl)phosphinic acid together with some tris(*p*-dimethylaminophenyl)-phosphine oxide and bis(*p*-dimethylaminophenyl)methane.[424–5] Hypophosphorous acid adds to olefins with free-radical catalysts giving phosphinic acids[443–4]:

$$H_2PO_2H + 2RCH{=}CH_2 \rightarrow (RCH_2CH_2)_2PO_2H$$

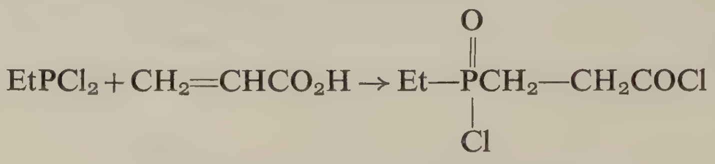
and to aldehydes giving bis(α-hydroxyalkyl)phosphinic acids. Sodium hypophosphite and formaldehyde react at 130°–135° giving sodium bishydroxymethylphosphinate[1734]:

$$NaH_2PO_2 + HCHO \xrightarrow{135^\circ} (HOCH_2)PO_2Na \xrightarrow{HCl} (HOCH_2)_2PO_2H \qquad (93\%\ \text{yield})$$

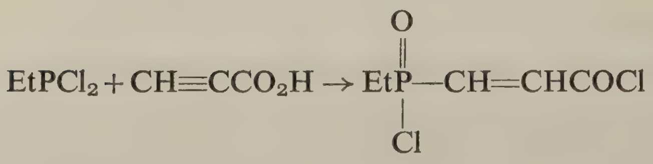
A comparatively new method of forming carbon–phosphorus bonds is the interaction of phosphorus trichloride, aluminium trichloride and olefins.[1461] By this method 1,1,2,3,3-pentamethyltrimethylenephosphinic acid chloride may be obtained from 2,4,4-trimethyl-2-pentene followed by partial hydrolysis of the intermediate complex; complete hydrolysis yields the corresponding acid:



Ethyl dichlorophosphine adds to the double bond of unsaturated acids such as acrylic acid and propiolic acid to form phosphinyl chloride derivatives which can be hydrolyzed to the acids or esterified[2391–2]:



$$EtPCl_2 + CH_2{=}CHCO_2H \rightarrow Et{-}\underset{\displaystyle Cl}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}CH_2{-}CH_2COCl$$

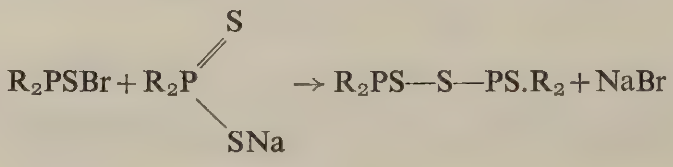


$$EtPCl_2 + CH{\equiv}CCO_2H \rightarrow Et\underset{\displaystyle Cl}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}CH{=}CHCOCl$$

PHOSPHINIC ACID ANHYDRIDES

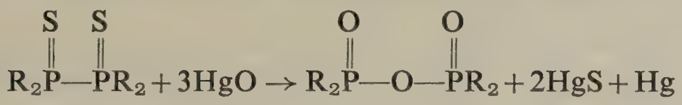
These have been prepared by the reactions[426, 1487, 1566]:

$$R_2POCl + R_2PO.OEt \xrightarrow{\text{heat}} R_2PO{-}OPO.R_2 + EtCl$$



$$R_2PSBr + R_2P\begin{matrix}{/\!\!/}S\\ \diagdown SNa\end{matrix} \rightarrow R_2PS{-}S{-}PS.R_2 + NaBr$$

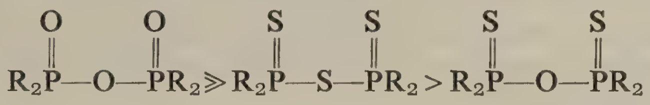
and from tetra-alkylphosphine disulphides by treatment with mercuric oxide[587, 1903]:



$$R_2\overset{\overset{S}{\|}}{P}-\overset{\overset{S}{\|}}{P}R_2 + 3HgO \rightarrow R_2\overset{\overset{O}{\|}}{P}-O-\overset{\overset{O}{\|}}{P}R_2 + 2HgS + Hg$$

Diphenylphosphinodithioic acid loses hydrogen sulphide on heating to give the trithioanhydride.[427]

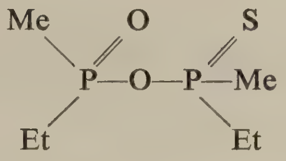
The oxygen compounds are much more readily hydrolyzed than tetra-alkyl pyrophosphates,[426] and react with alcohols giving equimolar amounts of acid and alkyl ester. In alkylpyrophosphinates the rates of hydrolysis of oxygen- and sulphur-containing compounds decreases in the order:

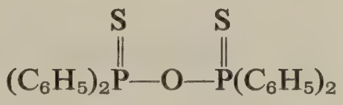


$$R_2\overset{\overset{O}{\|}}{P}-O-\overset{\overset{O}{\|}}{P}R_2 \gg R_2\overset{\overset{S}{\|}}{P}-S-\overset{\overset{S}{\|}}{P}R_2 > R_2\overset{\overset{S}{\|}}{P}-O-\overset{\overset{S}{\|}}{P}R_2$$

With respect to the R group the rate sequence is $C_3H_7 > C_2H_5$.[587]

The nuclear magnetic resonance spectra of dimethyl diethyl monothiopyrophosphinate and tetraphenyl dithiopyrophosphinate indicate the compounds to have the thiono structure[1566]:





$$(C_6H_5)_2\overset{\overset{S}{\|}}{P}-O-\overset{\overset{S}{\|}}{P}(C_6H_5)_2$$

Bis(thiophosphinyl) disulphides and trisulphides result from the action of iodine or sulphur dichloride respectively on the phosphinyldithioic acid.[586]

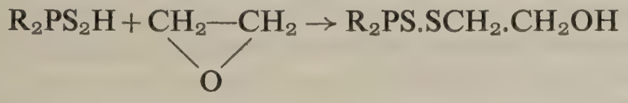
PHOSPHINIC ESTERS

These may be prepared by conventional methods from the phosphinyl halide

$$R_2POX \xrightarrow{NaOR'} R_2POOR'$$

and $$R_2PSX \xrightarrow{NaOR'} R_2PS.OR'$$

Esters of unsymmetrical acids have been obtained from esters of phosphonous acids by the Arbuzov reaction. Dithio esters are formed by the addition of the thio acids to ethylene oxide[429] or to electronegatively substituted olefins,[445] or by the reaction of the salts of the acid with alkyl halide[586, 2393]:



$$R_2PS_2H + CH_2{=}CHX \rightarrow R_2PS.SCH_2CH_2X \qquad (X = CN, CNO, CO_2R)$$

A number of esters of the type RR′PO.OR″ having an asymmetric phosphorus atom have been resolved.[417, 574, 589] Use of optically active *O*-methyl phenyl ethyl phosphinate has shown that, in methoxyl exchange with methoxide ion in methyl alcohol, each exchange involves inversion of configuration at the phosphorus atom.[591] Similarly, compounds $Me(\alpha\text{-}C_{10}H_8)POX$ (where $X = -SCH_2Ph$, Cl, F) react with methoxide ion giving the methyl ester with predominant inversion of configuration.[496, 590]

## DERIVATIVES OF PHOSPHOROUS ACID

### The Reaction of Phosphorus Trihalides with Hydroxy Compounds

Phosphorus trihalides are used both for the replacement of hydroxyl groups in alcohols with halogen groups and for the preparation of esters of phosphorous acid;

these two functions have been correlated, and the sequence of reactions which occurs has been studied by Gerrard and co-workers.[592–4, 596–601, 939]

Addition of an alcohol to phosphorus trihalide at 0° in the absence of a base results in rapid stepwise alkoxylation giving successively alkyl phosphorodichloridite, dialkyl phosphorochloridite, and trialkyl phosphite[592]:

$$\text{(1)} \qquad ROH + PCl_3 \rightarrow ROPCl_2 + HCl \qquad \text{(fast)}$$
$$\text{(2)} \qquad ROH + ROPCl_2 \rightarrow (RO)_2PCl + HCl$$
$$\text{(3)} \qquad ROH + (RO)_2PCl \rightarrow (RO)_3P + HCl$$

These reactions compete with dealkylation of the esters by hydrogen halide giving alkyl halide; the relative rates of dealkylation of the chloro esters by hydrogen chloride are $ROPCl_2 < (RO)_2PCl < (RO)_3P$[592]; and *n*-alkyl < *sec*-alkyl < *tert*-alkyl. For the corresponding bromo- and iodo-compounds with corresponding hydrogen halide the relative rates are[599]

$$HCl < HBr < HI.$$

With tributyl phosphite and hydrogen chloride at 0°C. the dealkylation is fairly fast[593]:

$$\text{(4)} \qquad (RO)_3P + HCl \rightarrow RCl + (RO)_2POH$$

the overall reaction becoming:

$$\text{(5)} \qquad 3ROH + PCl_3 \rightarrow (RO)_2POH + 2HCl + RCl$$

Gerrard[799] mentions only two exceptions to dealkylation of trialkyl phosphites according to Equation (4). These are $(Cl_3CCH_2O)_3P$[799] and $[(Cl_3C)_2CHO]_3P$,[798] which react with hydrogen chloride or bromide giving phosphorohalidite and alcohol. Further dealkylation of the dialkyl phosphite to monoalkyl phosphite and thence to phosphorous acid occurs. The rates of dealkylation are, for a given ester with respect to hydrogen halide, $HI > HBr \gg HCl$[593–4] and for a given halide with respect to the phosphite, $P(OR)_3 \gg (RO)_2POH > ROPO_2H_2$.

In reaction (4) phosphites derived from optically active alcohols such as 2-octanol give the alkyl halide (Cl, Br, I) with predominant inversion of configuration.[594, 596–8]

Dealkylation of di-*iso*propyl phosphite by HCl was studied by Campbell and Chadwick.[595] It was found that the phosphite forms with hydrogen chloride a complex having $\Delta H = 10{\cdot}7$ kcal./mole. Dealkylation proceeds by attack of free hydrogen chloride on this complex.

Phosphorus trifluoride is reported to react with alcohols giving organic phosphites,[842] the exact nature of which is unspecified.

### Phosphorohalidites, $(RO)_nPX_{3-n}$, $n = 1$ or 2, X = halogen

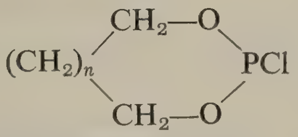
Alkyl phosphorodichloridites are generally prepared by the addition of an alcohol to a slight excess of phosphorus trichloride at room temperature.[824–5, 837, 1070] Generally a stream of inert gas is passed through the solution during and after the reaction to assist removal of hydrogen chloride before distillation. Alkyl phosphorobromidites have been obtained similarly by carrying out the reaction at −15°C.[601] Alkyl phosphorodiiodites have not been reported. Aromatic and sulphur-containing derivatives, $ArOPCl_2$, $ArSPCl_2$, $AlkSPCl_2$, have been obtained by similar methods at somewhat higher reaction temperatures[1] using phenol, thiophenol and alkyl mercaptan, respectively. Good yields of aryl phosphorodichloridites are obtained by treating phenols with an excess of phosphorus trichloride under reflux in the presence of anhydrous magnesium chloride catalyst.[1682] Trichloromethylsulphenyl chloride reacts with tetraphosphorus heptasulphide giving $Cl_3CSPCl_2$, together with

$Cl_3CSPSCl_2$ and $(Cl_3CS)_2PSCl$.[826] Elemental phosphorus and sulphenyl chlorides react to form a mixture of $RSPCl_2$, $(RS)_2PCl$, and $(RS)_3P$.[827]

Dialkyl phosphorochloridites[600] and dialkyl phosphorobromidites,[601] and the corresponding aryl and thiol derivatives, are obtained in poor yield by the addition of two equivalents of an alcohol, phenol or mercaptan, to phosphorus trihalide. Better yields are obtained by conducting the reaction in an inert solvent at low temperature in the presence of two equivalents of a tertiary organic base,[829, 1070] or by further alkylation of a phosphorochloridite with an alcohol in the presence of a tertiary base[532, 1070] or a sodium alkoxide[837] or by the equilibration of phosphorus trichloride and a trialkyl phosphite at room temperature[600, 1070]:

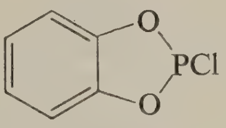
$$PCl_3 + 2ROH + 2B \rightarrow (RO)_2PCl + 2BHCl \qquad (B = \text{base})$$
$$ROPCl_2 + RONa \rightarrow (RO)_2PCl + NaCl$$
$$PCl_3 + 2P(OR)_3 \rightarrow 3(RO)_2PCl$$

1,2- 1,3- and 1,4-Glycols,[781, 796-7, 828] catechol[831, 877] and salicylic acid,[830] react with phosphorus trichloride giving fair yields of phosphorochloridites in which the phosphorus atom forms part of a 1,3,2-dioxaphospholane ring, compounds **I**, **II** and **III** respectively.

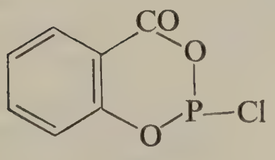


$n = 0, 1, 2$

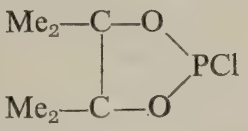
**I**



**II**



**III**

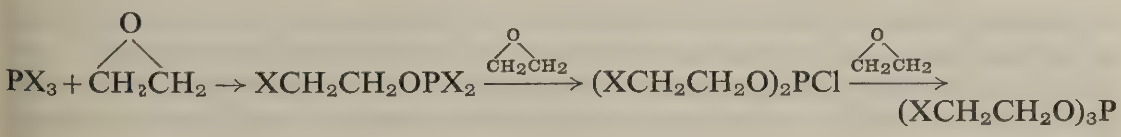


**IV**

$^1$H-Nuclear magnetic resonance of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, **IV**, indicates a relatively stable pyramidal stereochemical configuration about the phosphorus atom.[1082]

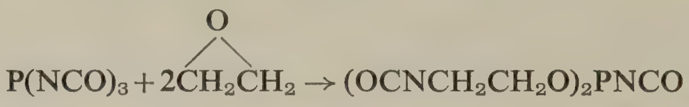
Equilibration in the systems $(PhO)_3P$–$PCl_3$,[833] $(EtO)_3$–$PCl_3$[1683] and $(EtS)_3P$–$PCl_3$[1713] has been studied by Van Wazer. In the triphenyl phosphite system no reaction takes place during 15 hr. at room temperature; at equilibrium, after 66 hr. at 180°, nuclear magnetic resonance showed a mixture of products whose molar percentages were greater than expected for a purely random distribution of chloro- and phenoxy-groups. Thus, starting with a mixture having a 1 : 1 molar ratio of –Cl to –OPh groups the relative amounts of $PCl_3$, $PhOPCl_2$, $(PhO)_2PCl$ and $(PhO)_3P$ at equilibrium were 1 : 7 : 7 : 1. In the $PCl_3$–$P(OEt)_3$ system exchange occurs readily; equilibrium product determination shows that the intermediates are more stable than would be expected from a statistical distribution, the ratios $(EtO)_3P : (EtO)_2PCl : EtOPCl_2 : PCl_3$ being 1 : 7 : 7 : 1. In the $P(SBu)_3$–$PCl_3$ system the equilibrium ratios, after 48 hr. at 120°, of $(BuS)_3P : (BuS)_2PCl : BuSPCl_2 : PCl_3$ are 0·7 : 7 : 8·5 : 3.

2-Halogenoethyl phosphorodihalidites and phosphorohalidites have been obtained by the reaction of ethylene oxide with phosphorus trichloride[834, 1283] and tribromide[835]:



$$PX_3 + \overset{O}{CH_2CH_2} \rightarrow XCH_2CH_2OPX_2 \xrightarrow{\overset{O}{CH_2CH_2}} (XCH_2CH_2O)_2PCl \xrightarrow{\overset{O}{CH_2CH_2}} (XCH_2CH_2O)_3P$$

The pseudohalogen compound, phosphorus triisocyanate, reacts similarly with ethylene oxide giving bis- (2-cyanoethyl)phosphorus(III) *iso*cyanate[836]:



$$P(NCO)_3 + 2\overset{O}{CH_2CH_2} \rightarrow (OCNCH_2CH_2O)_2PNCO$$

Phosphorofluoridites $(RO)_nPF_{n-3}$ have been prepared by metathetical reactions from the corresponding chloridites using reagents such as sodium fluoride, potassium fluosulphinate, antimony(III) fluoride or arsenic(III) fluoride.[838, 841, 906, 935, 1072] Diethyl phosphorofluoridite can be obtained by reaction of ethyl alcohol with phosphorus dichlorofluoride.[1070] The fluoridites form Ni(0) and Mo(0) complexes such as $Ni(n\text{-}C_3H_7OPF_2)_4$ and $Mo(CO)_3.(n\text{-}C_3H_7OPF_2)_3$ by displacement of carbon monoxide from nickel or molybdenum carbonyl.[838]

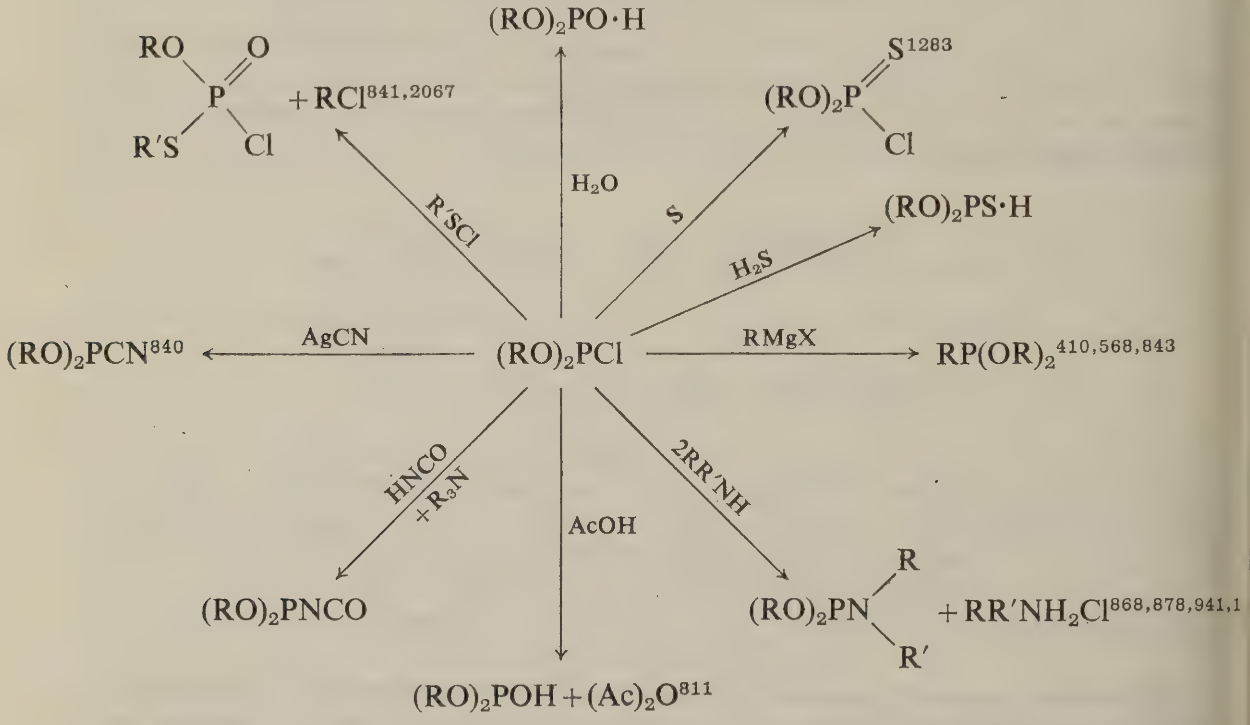
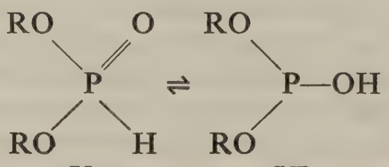


CHART XII.—Some typical reactions of phosphorochloridites

### Dialkyl Hydrogen Phosphonates and Dialkyl Hydrogen Phosphonothionates

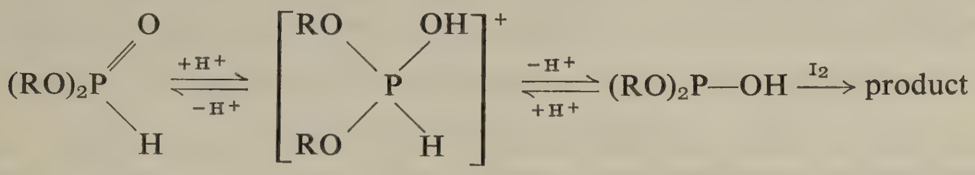
The structure of dialkyl phosphites was a subject of considerable controversy in the early days of organophosphorus chemistry. It is now generally agreed, on the basis of infra-red,[613] Raman,[611] ultra-violet,[612] P-nuclear magnetic resonance[602] and H-nuclear magnetic resonance[603] spectroscopy, that the compounds exist predominantly in the phosphonate structure **V** with no detectable amount of the phosphite form **VI**:



**V** **VI**

However, many reactions of the compounds which appear to proceed through the phosphite form, such as the slow reaction with sulphur and phenyl azide,[615] are difficult to explain without assuming the existence of a tautomeric equilibrium between the two forms. In a valuable review of the chemical and kinetic evidence, Doak and Freedman[604] conclude that the dialkyl phosphites do exist as equilibrium mixtures of the two tautomeric forms with an overwhelming preponderance of V.

Nylén[607] showed the rate of oxidation of diethyl phosphite by iodine or bromine to be proportional to the concentration of (RO)$_2$POH but of zero order with respect to halogen at high halogen concentration. He further found the reaction to be subject to general acid-base catalysis and proposed a prototropic shift as the rate-determining step in the oxidation:



In agreement with this Luz and Silver showed the rate of oxidation and rate of exchange of the P–H hydrogen in diethyl phosphite in acid solution to be the same.[605–6] Using (EtO)$_2$PO.H and (EtO)$_2$PO.D they demonstrated a kinetic isotope effect, $k^{\mathrm{H}}/k^{\mathrm{D}} = 4$, indicating the reaction to proceed by a fast pre-equilibrium protonation of the P=O group followed by slow rate-determining fission of the P–H bond. Deuterium exchange between (BuO)$_2$PO.H and *n*-butyl alcohol-*D* is subject to acid-base catalysis; in neutral solution the exchange rate is several orders lower than for the catalyzed reactions, and Bailey and Fox[614] conclude that if a tautomeric equilibrium exists in the neutral solution the concentration of enol form is of the order of $10^{-4}$ per cent. In the base-catalyzed exchange reaction removal of the P–H proton has been suggested to be the rate-controlling step.[614]

Dialkyl phosphites have much higher boiling points than the corresponding trialkyl phosphites. Many workers have cited this fact, together with results of Raman and infra-red spectroscopy, viscosity and parachor measurements, and M.W. determination to show that the compounds are associated in solution, with hydrogen-bonding usually suggested as the linkage. After carefully reviewing the work, Doak and Freedman[604] concluded that there is no convincing evidence for hydrogen-bonding but that in the liquid state, in the absence of solvent, association occurs through dipole–dipole interaction of the phosphoryl groups.

The proton nuclear magnetic resonance,[608] infra-red spectrum,[609] and molecular refraction of dialkyl hydrogen phosphorothionates confirm the phosphorothionate structure. The possibility of the existence of a tautomeric equilibrium as in dialkyl phosphites was suggested by Kabachnik *et al.*,[610] who concluded that the tautomeric shift to (RO)$_2$P–SH is relatively small.

Chemical evidence alone suggests that the equilibrium enol concentration decreases in the series (PhO)$_2$PO.H > (AlkO)$_2$PO.H > (AlkO)$_2$PS.H. Thus, in the absence of solvent, diphenyl phosphite reacts with sulphur giving diphenyl phosphonothioate[615]; with diethyl phosphite the reaction proceeds to 7% of completion in 8–9 hr. at 100°–105°[636] and with diethyl hydrogen phosphonothionate no reaction takes place in 5 hr. at 100°.[610] Relatively basic solvents have been suggested to favour formation of the enol form of the phosphite; the evidence advanced to support this idea is the increasing degree of sulphuration of diethyl phosphite in a series of solvents of increasing basicity; the solvent and percentage yields of (EtO)$_2$PSOH are: none, 7%; EtOH, 8·8%; PhMe, 10·6%; C$_6$H$_6$, 12·6%; Et$_2$O, 13·5%; dioxan, 68–73%.[616]

### PREPARATION OF DIALKYL AND DIARYL HYDROGEN PHOSPHONATES

The most generally used method of preparing dialkyl compounds is by the interaction of three or more moles of an alcohol with phosphorus trichloride (Equation (4), p. 982). Various solvents, such as benzene, carbon tetrachloride, methyl chloride[617] or butane,[618] have been suggested, particularly for the preparation of lower alkyl and the *iso*propyl compounds where effective cooling is more difficult and high reaction temperatures must be avoided to prevent dealkylation of the phosphite by hydrogen chloride. The heat of reaction of phosphorus trichloride with methanol is 42 kcal./mole in the reaction zone and 32 kcal./mole when all the hydrogen chloride has been removed.[617] With *iso*propanol the heat of reaction is 42 kcal./mole; the heat of solution of hydrogen chloride in the phosphite to give (*iso*-$C_3H_7O)_2PO.H.HCl$ is 10·7 kcal./mole.[595, 619] Continuously operating processes for the preparation of dialkyl phosphites have been described.[617, 619]

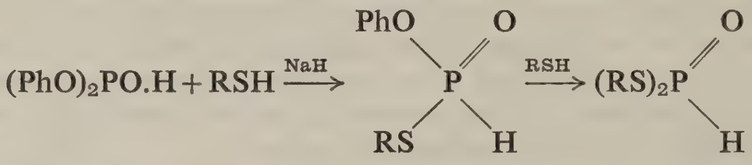
Tertiary organic bases (2 moles) have been used to prepare compounds such as dibenzyl phosphite which are very readily dealkylated by hydrogen chloride[620]:

$$3PhCH_2OH + PCl_3 + 2R_3N \rightarrow (PhCH_2O)_2PO.H + PhCH_2Cl + 2R_3N,HCl$$

A modification of the standard procedure which avoids the loss of one mole of alcohol as alkyl chloride is the reaction[621–2, 1088]:

$$2ROH + H_2O + PCl_3 \rightarrow (RO)_2PO.H + 3HCl$$

Dialkyl phosphites derived from higher molecular-weight alcohols[625–7] and mixed alkyl phosphites[624] have been prepared by transesterification of the lower dialkyl phosphites with higher alcohols (review, ref. 2398). The reaction proceeds smoothly in the presence of a catalyst such as a metal alkoxide or amide or phosphoric acid. Van Wazer finds that equilibration occurs between dimethyl or diethyl phosphite with acid but not basic catalysts. The equilibrium constant is close to the random value.[1713] Diphenyl phosphite undergoes transesterification with alcohols at about 100°,[628] compared with temperatures of up to 160° required for dialkyl phosphites. Transesterification of diphenyl phosphite with mercaptans in the presence of sodium hydride catalyst has been used to prepare *O*-phenyl, *S*-alkyl hydrogen phosphonothiolates and *S,S*-dialkyl hydrogen phosphonodithiolates[846]:



$$(PhO)_2PO.H + RSH \xrightarrow{NaH} (PhO)(RS)P(=O)H \xrightarrow{RSH} (RS)_2P(=O)H$$

Dialkyl phosphites of higher molecular weight are also obtained in good yield by the direct esterification of phosphorous acid with alcohol using catalysts such as zinc chloride, sulphuric acid or potassium acetate.[566, 623]

Diphenyl phosphite and bis-2-chloroalkyl phosphites are best prepared by the proportionation of the corresponding tertiary phosphite with phosphorous acid[632, 1073]:

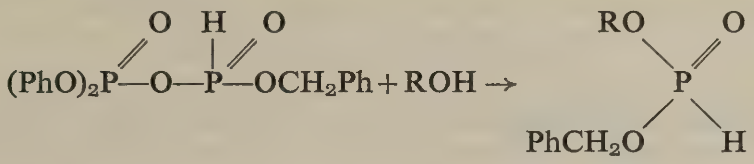
$$2(PhO)_3P + H_3PO_3 \rightarrow 3(PhO)_2PO.H$$

### MISCELLANEOUS METHODS

Dialkyl phosphites have been prepared by introducing oxygen into a suspension of white phosphorus in an alcohol,[629] by the reaction of diazoalkanes such as diazomethane[630] or phenyldiazomethane[620] with phosphorous acid and by the alkylation of salts of phosphorous acid, e.g., $Na_2HPO_3$, with dimethyl sulphate.[631] Bis-trialkylsilyl phosphites can be prepared by the slow distillation of a mixture of a trialkylmethoxysilane with $H_3PO_3$,[1074] or by esterification of phosphorous acid with hexa-alkyl disiloxane[2399]:

$$CH_3OSiR'_3 + H_3PO_3 \rightarrow (R'_3SiO)_2PO.H + CH_3OH\uparrow$$
$$H_3PO_3 + (Me_3Si)_2O \xrightarrow{ZnCl_2} (Me_3SiO)_2PO.H + H_2O\uparrow$$

Todd and co-workers[1598] showed that solutions of *O'*-benzyl-*O,O*-diphenyl phosphoric anhydride, formed by the reaction of monobenzyl phosphite with diphenyl phosphorochloridate or tetraphenyl pyrophosphate, react with alcohols giving alkyl benzyl phosphites:



$$(PhO)_2P(O){-}O{-}P(O)(H){-}OCH_2Ph + ROH \rightarrow (RO)(PhCH_2O)P(O)H$$

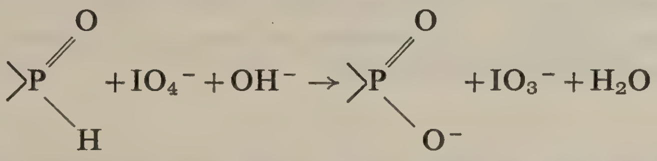
Benzyl nucleoside-5′-phosphites were used as intermediates for the synthesis of nucleosides-5′-pyro- and tri-phosphates.[1589, 1599]

## Reactions of Dialkyl Phosphites

Dialkyl phosphites are extremely versatile reagents which undergo reactions in which the phosphorus atom can act as a nucleophilic, electrophilic or free-radical centre. Many of the reactions involve the P–H hydrogen atom and are in general base-catalyzed. In this respect the hydrogen atom may be considered roughly comparable in its chemical reactions with the hydrogen atoms of the active methylene groups of malonic ester or ethyl acetoacetate.

### OXIDATION

Dialkyl phosphites are stable to atmospheric oxidation; amongst the reagents suggested for their oxidation to dialkyl phosphates are aqueous potassium permanganate,[708] aqueous chloramine-*T*,[637] nitrogen tetroxide,[707, 1117–8] lead tetra-acetate[889] and peracids.[1116] Brown and Hammond[1114] investigated the oxidation of dibenzyl phosphite by permanganate, periodate, iodate and hypochlorite: of these the preferred reagent was periodate in mildly alkaline solution which reacts according to the equation:

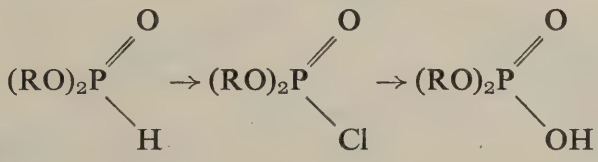


$$>P(O)H + IO_4^- + OH^- \rightarrow >P(O)O^- + IO_3^- + H_2O$$

One of the most successful methods for preparing dialkyl phosphates from the corresponding hydrogen phosphonate is oxidation with nitric oxide[638, 862]:

$$(RO)_2PO.H + NO \rightarrow (RO)_2PO_2H$$

Reaction with nitrosyl chloride in the presence of pyridine yields the corresponding tetra-alkyl pyrophosphate.[1077, 1542] An indirect method of oxidation to dialkyl phosphate involves chlorination to the phosphorochloridate followed by hydrolysis:



$$(RO)_2P(O)H \rightarrow (RO)_2P(O)Cl \rightarrow (RO)_2P(O)OH$$

### HALOGENATION

The dialkyl phosphites are readily chlorinated by elemental chlorine[706] or by sulphuryl chloride with or without solvent to give high yields of the corresponding dialkyl phosphorochloridates:

$$(RO)_2PO.H + SO_2Cl_2 \rightarrow (RO)_2PO.Cl + SO_2 + HCl$$

Chlorination with reagents such as *N*-chlorosuccinimide[1599] and *N*,*N*-dichlorobenzene sulphonamide[671] similarly yields the phosphorochloridate, but sulphur dichloride[709-10] and dimethylaminosulphenyl chloride[710,1078] (usually with a neutralizing agent such as pyridine) give a tetra-alkyl monothiopyrophosphate. Sulphur monochloride gives bis-dialkoxy-phosphinodisulphides,

$$(RO)_2PO—S—S—PO.OR_2{}^{1186}$$

Direct bromination with elemental bromine is unsatisfactory owing to the ready dealkylating action of the hydrogen bromide produced[902]; the dialkyl phosphorobromidate may, however, be prepared using *N*-bromosuccinimide.[639] Practically no reaction takes place at room temperature between dialkyl phosphites and iodine owing to the reduction of the phosphoroiodidate with hydrogen iodide,[700] $(RO)_2PO.H+I_2 \rightleftharpoons (RO)_2PO.I+HI$. For this reason the dialkyl phosphoroiodidates have been prepared by the action of iodine on the corresponding trialkyl phosphites.[700]

Pseudohalogens behave like chlorine, thiocyanogen forming dialkyl phosphorothiocyanatidate, $(RO)_2PO.NCS$.[640]

### REACTION WITH CARBONYL COMPOUNDS

Dialkyl α-hydroxy phosphonates are formed by the addition of dialkyl phosphites to aldehydes and ketones. Generally a basic catalyst[503,646,1685] has been used to catalyze the reaction, although free-radical catalysis has been reported.[645] Reaction with active aldehydes such as chloral will occur in the absence of a catalyst.[641,644,908,1192] With α-unsaturated aldehydes the products are the expected dialkyl 1-hydroxy-2-vinyl phosphonates,[642] but α-unsaturated ketones generally undergo primary addition of the dialkyl phosphite to the C=C double bond giving a γ-keto-phosphonate which may undergo reaction with a second molecule of dialkyl phosphite at the carbonyl group.[643] Keten and dialkyl phosphites react in the presence of boron trifluoride or sulphuric acid catalyst giving 1-acetoxy-vinyl phosphonates.[748] Diacetyl forms the expected 1-hydroxy-2-keto-phosphonate if the reaction is conducted at 100°, but at higher temperatures the product is an isomeric phosphate.[665] These reactions are shown in Chart XIII.

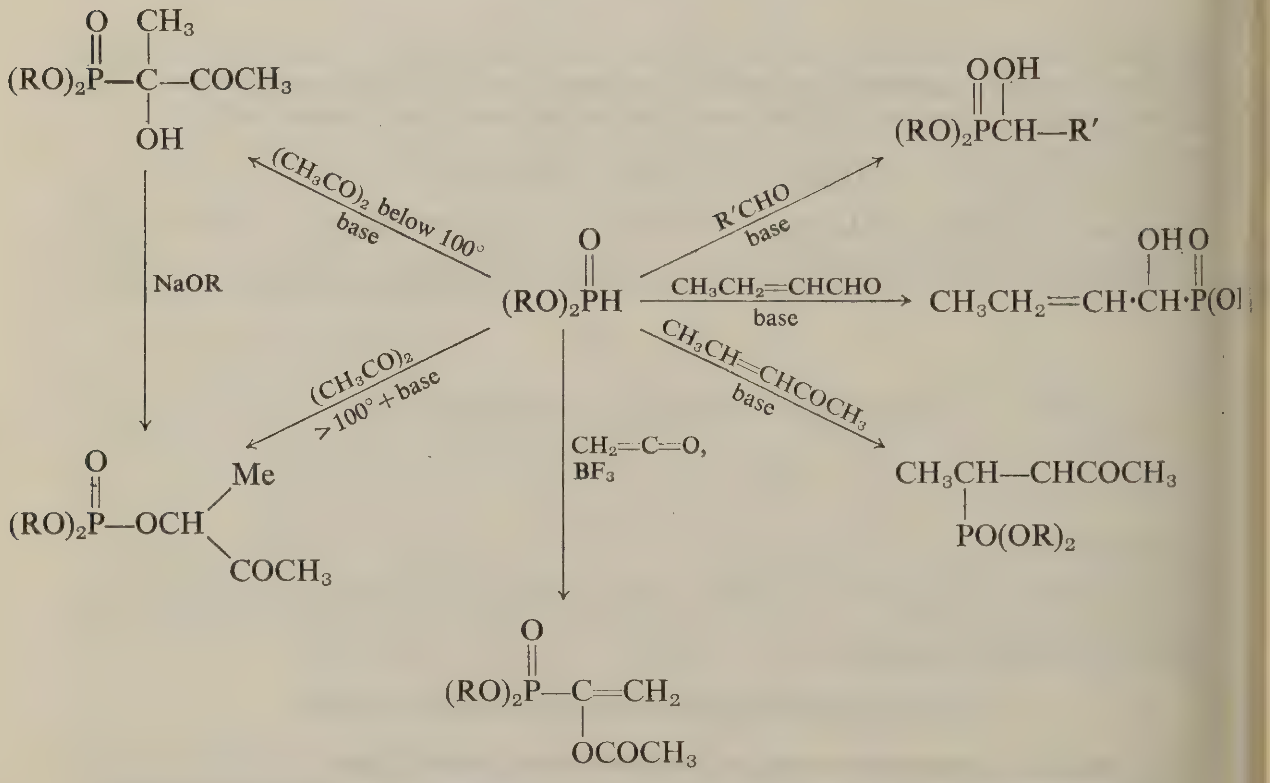
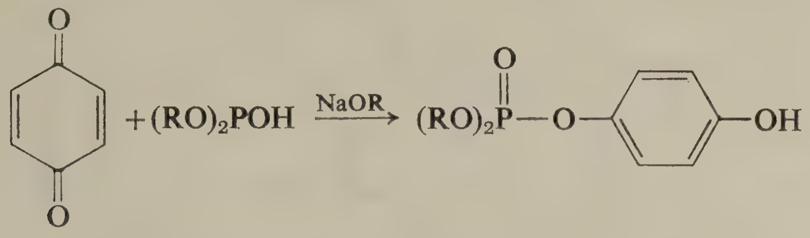


CHART XIII.—Some reactions of dialkyl phosphites with carbonyl compounds

Orthoformic esters and dialkyl phosphites react without catalyst to form dialkyl dialkoxymethylphosphonates[2059]:

$$(RO)_2POH + CH(OR')_3 \xrightarrow{182°} (RO)_2PO.CH(OR')_2 + ROH$$

*p*-Benzoquinone reacts vigorously with dialkyl phosphites in the presence of sodium alkoxide catalyst to form dialkyl *p*-hydroxyphenyl phosphates[679]:



Naphthaquinone and chloranil[680] behave similarly.

With salts of dialkyl phosphite, carbonyl sulphide and carbon disulphide form salts of dialkyl phosphorothiocarbonic and dithiocarbonic acids, respectively; these can be isolated by conversion to their methyl esters by reaction with methyl iodide[750]:

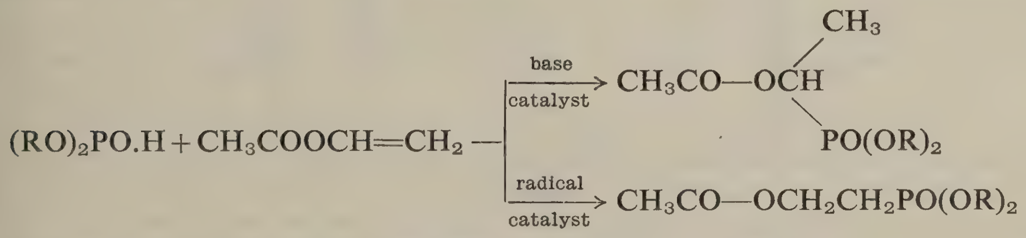
$$(RO)_2PONa + CS_2 \rightarrow (RO)_2PO.CS_2Na \xrightarrow{MeI} (RO)_2PO.CS.SMe$$

ADDITION TO UNSATURATED COMPOUNDS

The addition of dialkyl phosphites to non-activated olefins to form dialkyl alkylphosphonates takes place only in the presence of a free-radical catalyst. Examples of such olefins are simple alkenes[763] such as octene-1,[764,766] alkyl oleates,[658] $Et_3SiCH_2CH_2CH{=}CH_2$,[572] diallyl,[1091] and vinyl ethers.[1091,2400] $\gamma$-Radiation-induced additions of phosphites to a number of olefins are reported.[1688,2401-2]

$$R'CH{=}CH_2 + (RO)_2PO.H \xrightarrow[\text{catalyst}]{\text{radical}} R'CH_2CH_2PO(OR)_2$$

Olefins in which the C=C double bond is activated by an adjacent electron-attracting group, such as CO, CN, and $CO_2R$, undergo base-catalyzed addition of dialkyl phosphites, wherein the addition is similar to a Michael reaction and in a sense opposed to Markownikov's rule[648,682]; 2-substituted ethylphosphonates are formed. Generally, the attachment of substituent groups at the double bond slows down the reaction and necessitates the use of larger amounts of catalyst. In a number of cases the addition reactions have been carried out with radical-catalysts to form a product the same as that obtained in the base-catalyzed reaction.[765,1686] However, McConnell and Coover[1090] showed that with vinyl acetate the reactions proceed as shown below:



$$(RO)_2PO.H + CH_3COOCH{=}CH_2 \begin{cases} \xrightarrow[\text{catalyst}]{\text{base}} CH_3CO{-}OCH(CH_3)PO(OR)_2 \\ \xrightarrow[\text{catalyst}]{\text{radical}} CH_3CO{-}OCH_2CH_2PO(OR)_2 \end{cases}$$

Tetrafluoroethylene reacts with diethyl phosphite and benzoyl peroxide catalyst in an autoclave to form diethyl polyfluoroalkyl phosphonates, $H(CF_2CF_2)_nPO(OEt)_2$ where $n$ has an average value of 3.[1092,1477] $\gamma$-Radiation-induced addition of $(RO)_2POH$ to chlorofluoro-olefins proceeds:

$$(RO)_2PO.H + CFX{=}CX_2 \xrightarrow{\gamma\text{-radiation}} HX_2C{-}CFX{-}PO(OR)_2$$

(X = F or Cl, R = Me, Et, *n*-Pr)

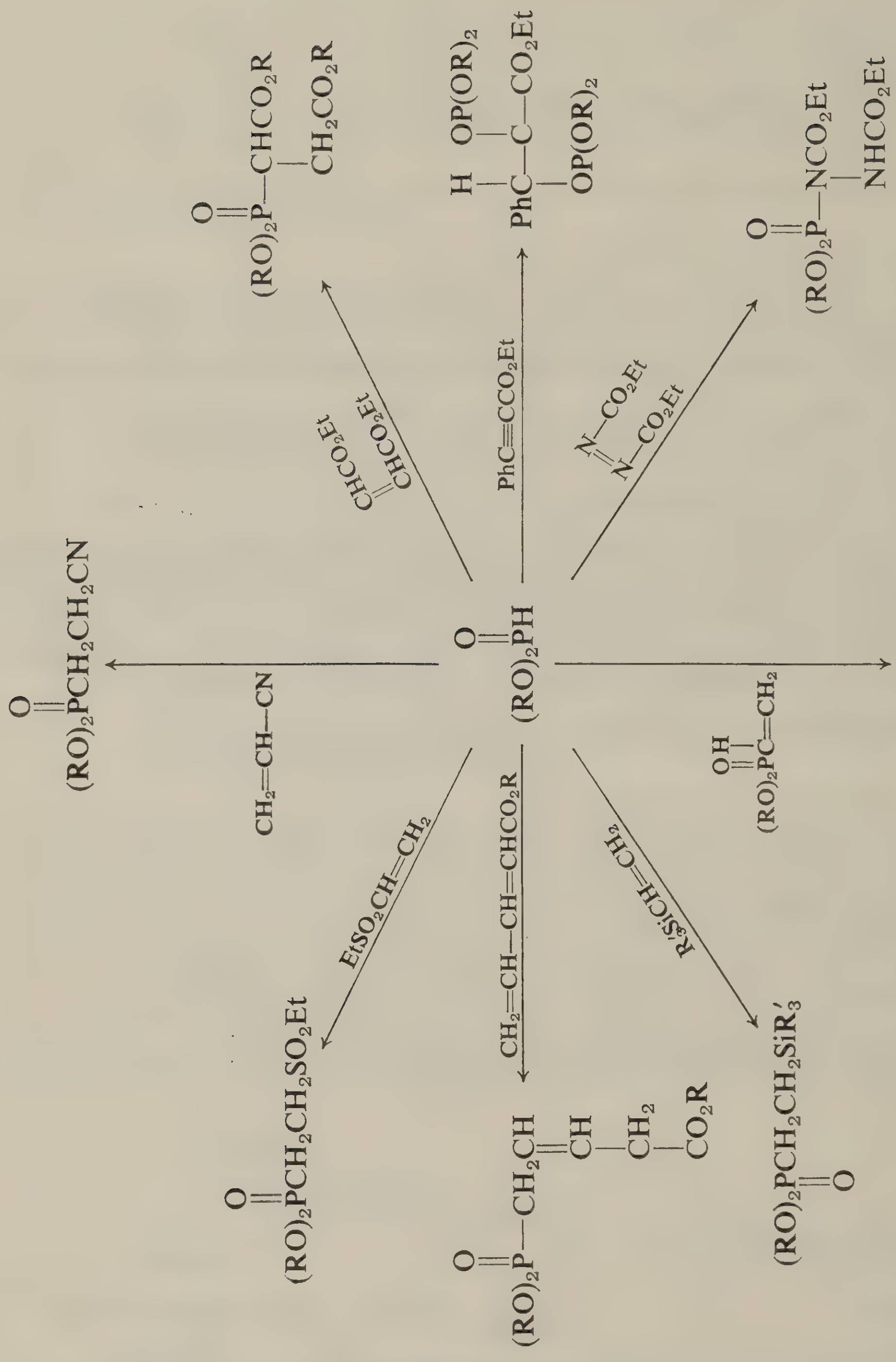

$(RO)_2P(=O)H$
$CH_2{=}CH{-}CN$
$(RO)_2P(=O)CH_2CH_2CN$
$CHCO_2Et{=}CHCO_2Et$
$(RO)_2P(=O){-}CHCO_2R{-}CH_2CO_2R$
$PhC{\equiv}CCO_2Et$
$PhC(H){-}C(OP(OR)_2)(OP(OR)_2){-}CO_2Et$
$N(CO_2Et){=}N(CO_2Et)$
$(RO)_2P(=O){-}NCO_2Et{-}NHCO_2Et$
$(RO)_2P(=O)C(OH){=}CH_2$
$(RO)_2P(=O)CH_2CH_2P(=O)(OR)_2$
$R'_3SiCH{=}CH_2$
$(RO)_2P(=O)CH_2CH_2SiR'_3$
$CH_2{=}CH{-}CH{=}CHCO_2R$
$(RO)_2P(=O){-}CH_2CH{=}CH{-}CH_2{-}CO_2R$
$EtSO_2CH{=}CH_2$
$(RO)_2P(=O)CH_2CH_2SO_2Et$

CHART XIV.—Some reactions of dialkyl phosphites with unsaturated compounds

The apparent reactivity of the olefins is in the order:

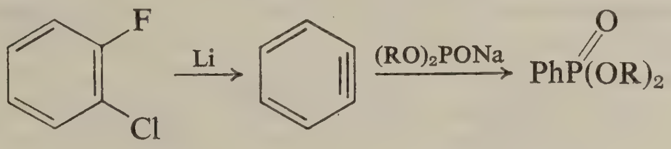
$$CFCl{=}CFCl > CFCl{=}CCl_2 > CF_2{=}CCl_2{}^{1687}$$

Examples of activated olefins which undergo base-catalyzed addition giving dialkyl 2-substituted ethyl phosphonates are as follows: esters of unsaturated acids such as maleic,[653, 1689] acrylic,[648, 1690] methacrylic,[653] cinnamic,[648, 650] benzylidenemalonic[652] and crotonic acids[648, 650]; α-unsaturated nitriles[662, 704] and amides,[653] unsaturated ketones[643, 664]; vinyl esters, such as vinyl acetate[651] and *iso*propenyl acetate[656]; esters of vinyl[655] and butadienyl phosphonic acid[1093]; vinyl sulphonic acid derivatives, such as ethyl vinyl sulphone,[649] dimethylaminovinyl sulphone[657] and vinyl sulphonyl fluoride[567] (no catalyst required); vinyl silicon compounds $CH_2{=}CHSiX_3$ ($X = R$ or OR,[659, 702] using a $(BuO)_2$ catalyst[1686]); α-nitro olefins,[649] and vinyl pyridines.[701]

Acetylenic esters such as methyl phenyl acetylenecarboxylate[654] and acetylenedicarboxylic ester[653] add two equivalents of dialkyl phosphite giving 1,2-(dialkoxyphosphinyl)ethane derivatives. Activated conjugated unsaturated compounds such as ethyl sorbate and hepta-3,5-diene-2-one undergo 1:4 addition giving 4-substituted but-2-enylphosphonates.[1093]

Similar addition reactions take place with Schiff's bases such as benzylideneaniline[663] and *N*-benzylidenepropylamine[660] and with *N*-methylenepiperidinium chloride,[705] giving substituted α-aminophosphonic esters. Diethyl azodicarboxylate[661] forms 1-dialkyloxyphosphinyl-1,2-dicarbethoxyhydrazine. Some base-catalyzed addition reactions are illustrated in Chart XIV.

The reaction of sodium diethyl phosphite with benzyne (formed *in situ* from the reaction of *o*-bromofluorobenzene with lithium) gives diethyl phenylphosphonate[749]; the same product is obtained in lower yield from triethyl phosphite. In a similar reaction ethyl diphenylphosphinite forms triphenylphosphine oxide:



FORMATION OF α-AMINOALKYL PHOSPHONATES

Fields[669] showed that dialkyl phosphites could be used in a Mannich-type reaction with an aldehyde and amine or a tetra-alkyl methylene diamine to give esters of α-aminoalkyl phosphonic acids. Thus, diethyl phosphite, formaldehyde, and diethylamine form diethyl diethylaminomethyl phosphonate:

$$(EtO)_2PO.H + HCHO + HNEt_2 \rightarrow (EtO)_2PO.CH_2NEt_2$$

Many variations of this basic reaction may be brought about by the use of other aldehydes, ketones, and amines. Of interest is the preparation of the aminobisphosphonate, $CH_3N[CH_2PO(OEt)_2]_2$, and aminotriphosphonate, $N[CH_2PO(OEt)_2]_3$, from the reaction of diethyl phosphite, formaldehyde, and methylamine or ammonia, respectively.[667]

In a related reaction the treatment of a dialkyl phosphite with an aldehyde or ketone and ammonia, usually in alcoholic media, at elevated temperature produces an α-aminophosphonate.[667–8, 681] Kabachnik *et al.* consider that in this reaction the α-hydroxyphosphonate is first formed at room temperature and reacts with ammonia on heating to give the α-amino compound[666, 670]:

$$(RO)_2PO.H + R'CHO \rightarrow (RO)_2PO.CH(OH)R' \xrightarrow[100°]{NH_3} (RO)_2PO.CH(NH_2)R'$$

THE TODD REACTION

Todd and his co-workers[672] found that a dialkyl phosphite, a polyhalogenated hydrocarbon, such as carbon tetrachloride, and an excess of ammonia or a primary or secondary amine react to form the corresponding dialkyl phosphoroamidate, a haloform, and the base hydrochloride:

$$(RO)_2PO.H + CCl_4 + 2R'_2NH \rightarrow (RO)_2PO.NR'_2 + CHCl_3 + R'_2NH,HCl$$

A number of halogenated hydrocarbons, such as $CBr_4$, $CHI_3$, $CHBr_3$, $CCl_3Br$, $C_2HCl_5$, $C_3Cl_8$, $C_4Cl_{10}$, $CCl_2{=}CH{-}CCl_3$, $Cl_2CH{-}CCl_3$, and $CFCl_2{-}CFCl_2$ are active, but $CHCl_3$, $CH_3{-}CCl_3$, $(CHCl_2)_2$, and $CCl_2{=}CCl_2$, are inactive.[673] Use of trichlorobromomethane gives particularly good yields of phosphoroamidates.[673] In the reaction between 2-aminoethanol and diethyl phosphite the reaction rate decreases in the following order with respect to halogenated hydrocarbon; $CCl_3Br > CCl_3CN \gg CCl_4 > CCl_3CO_2Et$.[676] The relative reaction rates of various amines with carbon tetrachloride and diethyl phosphite decrease in the series: diethylamine > tertiary butylamine > *cyclo*hexylamine > di-*iso*-propylamine > 2-aminoethanol.[676] Weakly basic amines, such as aniline, do not undergo the reaction except in the presence of a strong tertiary amine[672]; the reaction rate increases with the base strength of the tertiary amine and decreases with increasing size of the alkyl groups of the dialkyl phosphite.[675] It is believed that the reaction proceeds through intermediate formation of a dialkyl phosphorochloridate.[673, 675, 677] This view is supported by the isolation of diethyl phosphorochloridate in 81% yield from the reaction of diethyl phosphite, carbon tetrachloride and triethylamine.[677]

Various modifications of the Todd reaction have been carried out to form tetraalkyl pyrophosphate, dialkyl alkyl phosphate, dialkyl aryl phosphate, and dialkyl hydrazophosphonate. These are illustrated in Chart XV.

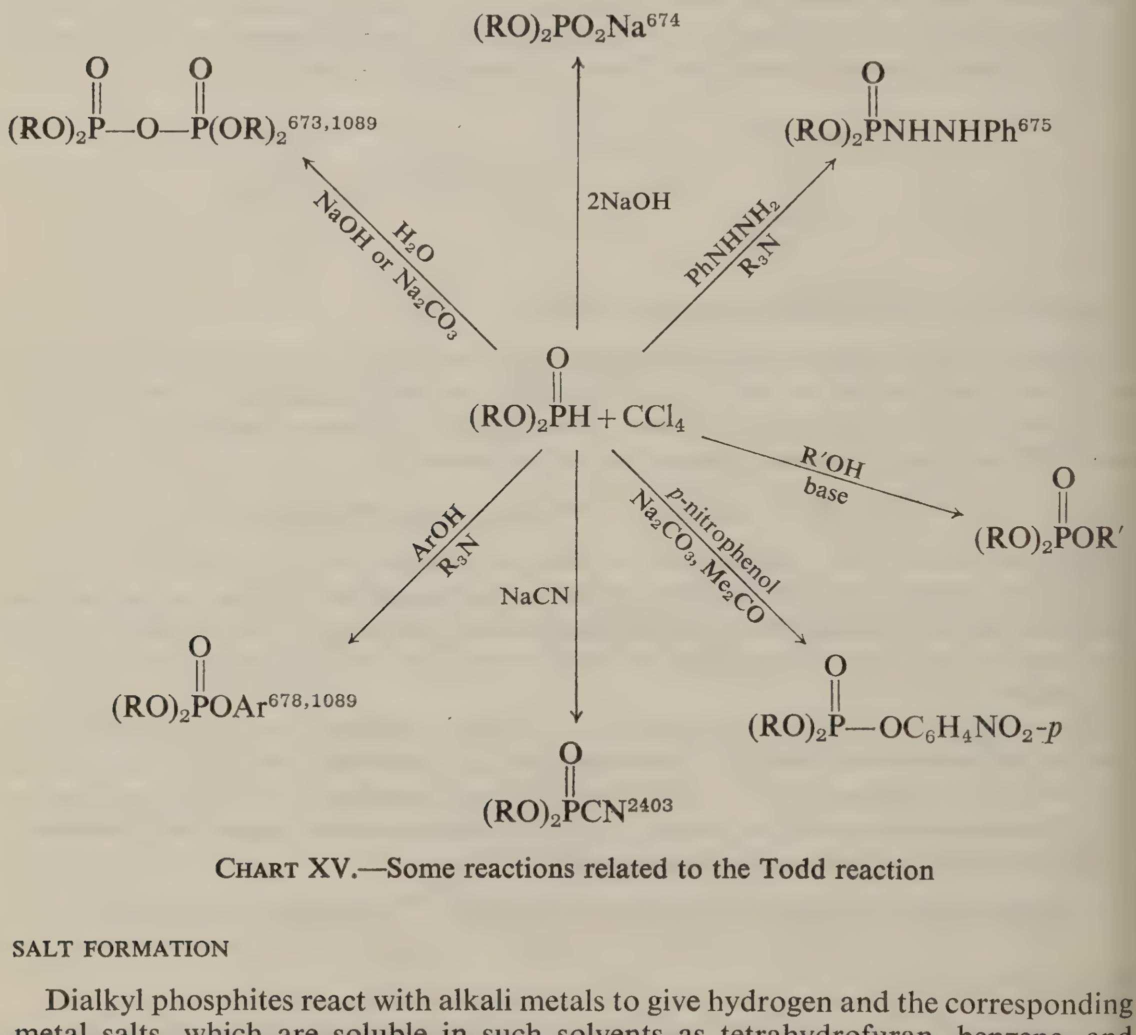


CHART XV.—Some reactions related to the Todd reaction

### SALT FORMATION

Dialkyl phosphites react with alkali metals to give hydrogen and the corresponding metal salts, which are soluble in such solvents as tetrahydrofuran, benzene, and petroleum ether. A better method of forming the sodium salt is treating the phosphite with sodium hydride in tetrahydrofuran solution[683]; this avoids the formation of phosphine by-products which result from reduction of the phosphite when the alkali metal is used. Salts may also be prepared using sodium alkoxides:

$$(RO)_2PO.H + M,\ MH,\ \text{or}\ MOR \rightarrow (RO)_2PO.M + \tfrac{1}{2}H_2,\ H_2,\ \text{or}\ ROH$$

Lithium and sodium salts are formed in low yield by heating a trialkyl phosphite with a lithium or sodium halide[684]:

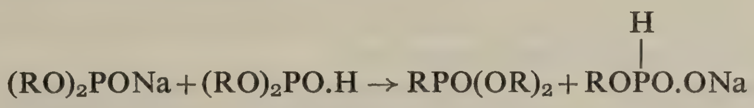
$$(RO)_3P + LiX \xrightarrow{\Delta} (RO)_2PO.Li + RX\uparrow$$

Magnesium salts have been prepared by treating a phosphite with magnesium in pyridine; halogenmagnesium salts are formed when a phosphite reacts with one equivalent of a Grignard reagent.[687] Silver salts may be prepared by treating the ester in aqueous solution, or suspension, with ammoniacal silver nitrate and then carefully neutralizing with nitric acid.[1691] Dialkoxyphosphinyl mercury salts are obtained from the dialkyl phosphites by treatment with a mixture of mercuric oxide and mercuric halide,[685] by treating the intermediate bis(dialkoxyphosphinyl) mercury with mercuric halide,[686] or by an Arbuzov-type reaction between a trialkyl phosphite and mercuric acetate[1083] :

$$(RO)_2PO.H + HgO \rightarrow [(RO)_2PO]_2Hg \xrightarrow{HgX_2} (RO)_2PO.HgX$$
$$(RO)_3P + Hg(OAc)_2 \rightarrow (RO)_2PO.HgOAc + ROAc$$

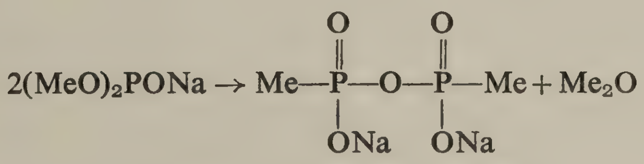
Stelling[690] examined the *X*-ray absorption spectrum of several salts of dialkyl phosphites. He concluded that the silver salt exists in the form $(RO)_2POAg$ and that the sodium salt exists in a form in which phosphorus is connected to four neighbouring atoms with sodium bonded to phosphorus. From a study of the infra-red spectrum of the lithium, sodium, potassium and silver salts of several dialkyl phosphites, Daasch[691] concluded that there is no evidence for the structure $[(RO)_2PO]Na$ and favours a structure having a covalent metal–oxygen bond.

Sodium salts of di-*n*-alkyl phosphites react with the parent dialkyl phosphites giving dialkyl alkyl phosphonates and sodium alkyl hydrogen phosphite[688-9]; the reaction proceeds at a significant rate above 60°[689]:



$$(RO)_2PONa + (RO)_2PO.H \rightarrow RPO(OR)_2 + RO\overset{\overset{H}{|}}{P}O.ONa$$

Analogous reactions of the secondary alkyl esters are much slower and proceed by *O*-alkylation; thus sodium di-*sec*-butyl phosphite reacts with the parent phosphite giving tri-*sec*-butyl phosphite and sodium *sec*-butyl hydrogen phosphite.[688] Sodium dimethyl phosphite decomposes at 50° giving disodium dimethyl pyrophosphonate and dimethyl ether[689]:



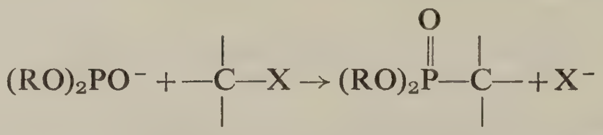
$$2(MeO)_2PONa \rightarrow Me{-}\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}{-}Me + Me_2O$$

Although the dialkyl phosphites themselves undergo little reaction with sulphur in the absence of solvent (p. 985), the alkali-metal salts react exothermically in inert media with sulphur or selenium giving salts of the corresponding dialkyl phosphorothionate or selenoate.[692] A similar reaction may be carried out with sulphur by adding gaseous ammonia[693–4] or a tertiary amine[1266] to a cooled mixture of dialkyl phosphite and sulphur:

$$(RO)_2PO.H + S + NH_3 \rightarrow (RO)_2PS.ONH_4$$

REACTIONS OF SALTS OF DIALKYL PHOSPHITES

Alkali-metal salts of dialkyl phosphites are strong nucleophiles; they participate in many displacement reactions at electrophilic carbon centres giving dialkyl phosphonates:



$$(RO)_2PO^- + -\overset{|}{\underset{|}{C}}-X \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}-\overset{|}{\underset{|}{C}}- + X^-$$

Reactions with numerous alkyl halides, with esters of sulphonic[683, 717] and sulphuric acids[715, 1105] and with Mannich bases[985] have been reported. The relative reaction rates towards primary *n*-alkyl compounds are $RI > RBr > ROSO_2C_6H_4\text{-}p\text{-}CH_3 > RCl$.[683] However, alkyl iodides are rarely used owing to the ready dealkylation by sodium iodide of the phosphonate ester product, giving alkyl iodide and sodium monoalkyl phosphonate.[716, 718]

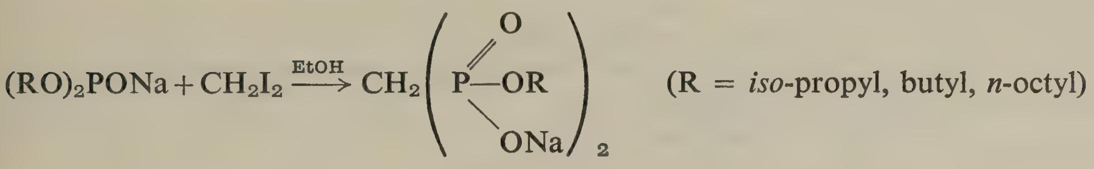
Generally, primary alkyl halides, particularly alkyl bromides,[712] give good yields of the corresponding phosphonate. Other primary halides which give the expected phosphonate (often in lower yield than obtained by the Arbuzov reaction) are amino-substituted halides such as 2-diethylaminoethyl chloride,[1187] trimethylsilylmethyl halides,[431, 732] arylmethyl halides such as benzyl chloride, benzyl bromide[719] and 7-chloromethyl benzanthracene[722]; halogenomethyl substituted heterocyclic compounds such as 2-chloromethyl pyridine[1699] and 2-chloromethyl quinoline[1094]; 1-(2-bromoethyl)piperidine[714]; tetrahydrofurfuryl bromide[714] and chloroacetonitrile.[727]

Secondary alkyl halides[364] and toluene sulphonates[717] give lower yields than those generally obtained from primary compounds. Diphenylmethyl bromide undergoes reductive coupling with sodium diethyl phosphite, giving a high yield of tetraphenylethane; the chloride gives but a poor yield of the expected phosphonate.[719] The reaction fails with *tert*-alkyl halides.[364]

Aryl halides such as chloro- and bromo-benzene, 2-chloro- and 2-bromopyridine fail to react; iodobenzene with sodium diethyl phosphite gives a moderate yield of sodium monoethyl phenyl phosphonate.[716] Successful reactions have been reported for a few heterocyclic halides such as 2-chloro-4,6-dimethylpyrimidine[740] and 2-chloroquinoline[741] giving dialkyl-4,6-dimethyl pyrimidyl phosphonate and dialkyl 2-quinolinyl phosphonate respectively.

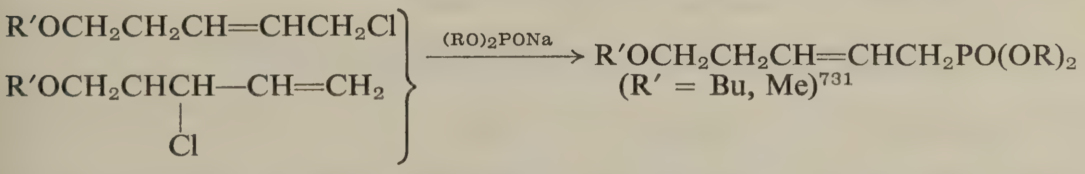
Ethyl chloroformate,[726] ethyl chloroacetate,[726–7] and $\alpha$- and $\gamma$-bromoethyl acetoacetates,[721] yield the expected phosphonic esters; dialkyl chloromethylphosphonates yield tetra-alkyl methylenediphosphonates.[723–4] Acetyl halides yield acetoxymethylenediphosphonates which result from addition of sodium dialkyl phosphite to the initially formed $\alpha$-ketophosphonate followed by acetylation.

Primary aliphatic $\alpha$-$\omega$ dihalides can react with two equivalents of sodium dialkyl phosphite giving a tetra-alkyl $\alpha$-$\omega$ alkyl diphosphonate,[723, 742] but the reaction of compounds having primary and secondary halogen atoms follows no set pattern. Thus, in $CNCHBr\text{–}CH_2Br$[713] the primary bromine atom is replaced and hydrogen bromide is then lost to yield $CNCH{=}CHPO(OR)_2$, but in $EtOCHCl\text{–}CH_2Cl$[744] the secondary chlorine atom is replaced giving $(EtO)_2OP(CHOEt)CH_2Cl$. Several 1,2-dihalogeno-compounds undergo dehalogenation. Ethylene dibromide and sodium diethyl phosphite give ethylene and a mixture of diethyl phosphite, triethyl phosphate, tetraethyl pyrophosphite, tetraethyl pyrophosphate, and tetraethyl ethylene-1,2-diphosphonate.[1714] 1,2-Dibromoethylbenzene gives styrene,[713] 9,10-phenanthrene dibromide gives phenanthrene,[720] and $(Me_2CBr)_2$ gives $Me_2C{=}CMe_2$ [713]; the nature of the phosphorus-containing product is not known. Methylene dihalides give generally poor yields of tetra-alkyl methylenediphosphonates,[723, 745] reaction of methylene di-iodide with sodium dialkyl phosphites gives moderate yields of disodium dialkyl methylenediphosphonates[1696]:



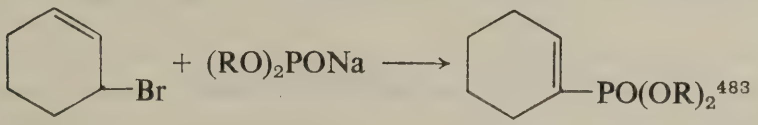
$$(RO)_2PONa + CH_2I_2 \xrightarrow{EtOH} CH_2\left(\begin{array}{l}\quad O\\ P—OR\\ \quad ONa\end{array}\right)_2 \quad (R = \textit{iso}\text{-propyl, butyl, } n\text{-octyl})$$

In the presence of an excess of dialkyl phosphites allyl halides react with sodium dialkyl phosphite giving dialkyl allylphosphonate[728] but with sodium dialkyl phosphite and allyl chloride (or allyl bromide) the products are propane-1,2-diphosphonates[728, 743]; this is possibly due to migration of the C=C double bond from the 2- to the 1- position in the initially-formed allyl phosphonate, followed by phosphite addition. Allylic rearrangements and carbon–carbon double- or triple-bond migration have been demonstrated in reactions of allylic halides and propargyl bromide:



$$\left.\begin{array}{l}R'OCH_2CH_2CH=CHCH_2Cl\\ R'OCH_2\underset{Cl}{\underset{|}{C}}HCH—CH=CH_2\end{array}\right\} \xrightarrow{(RO)_2PONa} R'OCH_2CH_2CH=CHCH_2PO(OR)_2$$

(R′ = Bu, Me)[731]

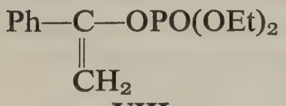


$CH\equiv C—CH_2Br + (RO)_2PONa \xrightarrow{THF} CH_3C\equiv C—PO(OR)_2$[2404]

α-Halogenocarbonyl compounds react anomalously. Thus, sodium dialkyl phosphite and ω-halogenoacetophenones can react to give either the expected phosphonate, **VII**, the rearranged vinyl phosphate ester, **VIII**, or the epoxyphosphonate, **IX**, or mixtures of these compounds, depending on the reaction conditions and the halogen atom replaced[729-30]:

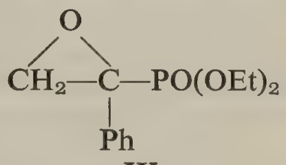
$PhCOCH_2PO(OEt)_2$

**VII**



$Ph—\underset{CH_2}{\underset{\|}{C}}—OPO(OEt)_2$

**VIII**



**IX**

The reaction of triarylmethyl halides with salts of dialkyl phosphites has been studied mainly by Arbuzov and co-workers. Early work with triphenylmethyl bromide and sodium dialkyl phosphites gave no phosphonate; the products isolated were triphenylmethane and a 'tetraethyl subphosphite', $((EtO)_2PO)_2$.[1095] Recently, *p*-alkoxy-substituted triphenylmethyl bromides have been shown to give high yields of the corresponding dialkyl phosphonates on reaction with sodium diethyl phosphate. Electron spin resonance measurements on the reacting solutions gave free-radical concentrations in the range $10^{15}$–$10^{17}$/ml. of solution.[1096] Silver salts of ethyl and *sec*-alkyl phosphites react immediately with triphenylmethyl halides giving dialkyl triphenylmethyl phosphites, but the silver salts of di-*n*-alkyl phosphites (except ethyl) yield dialkyl triphenylmethylphosphonates.[738]

In a manner formally similar to nucleophilic attack of dialkyl phosphite ions on carbon centres, the salts also participate in displacement reactions on sulphur, nitrogen,[1097] selenium, silicon,[732] and arsenic,[736] giving phosphorothiolate, phosphoroamidate, phosphoroselenoate, silicophosphonic and arsenophosphonic esters, respectively:

$$(RO)_2PONa + R'{-}SX \rightarrow (RO)_2PO.SR' + NaX$$

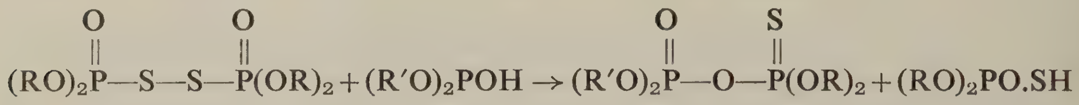
(X = SR,[735,737] Cl,[746] —CN,[747,1286] —NR$_2$,[1697] —SO$_2$R,[734] —SO$_2$Na[734])

$$(RO)_2PONa + R'_2AsCl \rightarrow (RO)_2PO.AsR'_2$$

$$(RO)_2PONa + R'_3SiCl \rightarrow (RO)_2PO.SiR'_3$$

$$(RO)_2PONa + R'NHBr \rightarrow (RO)_2PO.NHR' + NaBr$$

Dialkyl phosphites and dialkyl thionophosphites react with acyl disulphides in the absence of a base[735]:



$$(RO)_2\overset{O}{\overset{\|}{P}}{-}S{-}S{-}\overset{O}{\overset{\|}{P}}(OR)_2 + (R'O)_2POH \rightarrow (R'O)_2\overset{O}{\overset{\|}{P}}{-}O{-}\overset{S}{\overset{\|}{P}}(OR)_2 + (RO)_2PO.SH$$

In benzene solvent $(RO)_2POH$ and perhalogenomethyl mercaptans react to form *O*,*O*-dialkyl-*S*-perhalogenomethyl phosphorothioates:

$$(RO)_2POH + CCl_2FSCl \rightarrow (RO)_2PO.SCFCl_2 + HCl$$ [1695]

MISCELLANEOUS REACTIONS OF DIALKYL PHOSPHITES

In the presence of a base catalyst, dialkyl phosphites react with isocyanates[751,1224] and isothiocyanates[752-3] giving carbamoyl and thiocarbamoyl phosphonates, respectively:

$$(RO)_2PO.H + R'NCX \xrightarrow{\text{base}} (RO)_2PO.CX.NHR' \qquad (X = O, S)$$

When β-propiolactone and sodium diethyl phosphite react together both acyl–oxygen and alkyl–oxygen fissions occur giving diethyl α-keto-3-hydroxypropyl phosphonate and diethyl 2-carboxyethyl phosphonate, respectively.[755] When heated with a diethyl phosphite without catalyst acyl–oxygen fission predominates and the end-product, formed by further addition of dialkyl phosphite to the keto-compound, is tetraethyl 1,3-dihydroxypropylidene diphosphonate.[754]

Epoxy compounds react with sodium dialkyl phosphites[755] or dialkyl phosphites with boron trifluoride as catalyst[757] giving 2-hydroxyethylphosphonates. With a basic catalyst propylene oxide gives a diphosphonate. This may result from dehydration of the initially-formed hydroxypropylphosphonate to the propenephosphonate followed by addition of dialkyl phosphite.[656]

Aryl and heterocyclic diazonium salts and dialkyl phosphites form highly coloured dialkyl azophosphonates[758] which may be converted to the corresponding hydrazo-compounds by a variety of reducing agents[759]:

$$ArN_2^+X^- + (RO)_2POH \xrightarrow{\text{NaOAc}} ArN{=}N{-}PO(OR)_2 \xrightarrow{\text{Zn/HOAc}} ArNH{-}NHPO(OR)_2$$

Dialkyl phosphites react with carboxylic acids without catalysts giving high yields of corresponding carboxylic ester and phosphorous acid; both alkyl groups on the dialkyl phosphite can be utilized[938]:

$$(RO)_2POH + 2R'CO_2H \rightarrow 2R'CO_2R + H_3PO_3$$

Phenols yield the alkylphenyl ether.

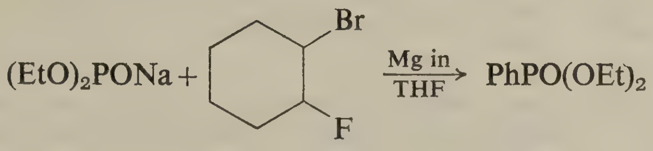
The alkylating properties of dialkyl phosphites are also exhibited in reactions with various sulphur compounds; thus thiourea gives an *S*-alkyl *iso*thiouronium monoalkyl phosphite,[760] and ammonium thiocyanate an alkyl isothiocyanate[762]; xanthates form the esters.[761]

Orthoformates and the lower dialkyl phosphites react to form acetals of formylphosphonic esters[1694]:

$$(RO)_2PO.H + CH(OR')_3 \rightarrow (RO)_2PO.CH(OR')_2 + R'OH$$

Diethyl phosphite and methyl benzoate react in the presence of di-*tert*-butyl peroxide to form diethyl *iso*-butyl phosphonate and diethyl (*p*-carbomethoxyphenyl) phosphonate.[1708] The reaction has been extended to polycyclic aromatic and heterocyclic compounds, such as naphthalene, anthracene, phenanthrene, dibenzofuran, and carbazole, to give the corresponding phosphonic esters in 51–96% yield.[1709]

Diethyl phenylphosphonate is formed by the interaction of sodium diethyl phosphite or triethyl phosphite with benzyne generated *in situ* by the action of magnesium on *o*-bromofluorobenzene in tetrahydrofuran solvent[749]:



### Dialkyl Hydrogen Phosphonothionates (dialkyl thionophosphites), $(RO)_2PS.H$

These compounds, in contrast to the dialkyl phosphites, are not easily prepared, and methods of synthesis have been published only during the last decade. Dialkyl hydrogen phosphonothionates are prepared (*a*) in low yield (*ca.* 20%)[609] admixed with a variety of other sulphur-containing organophosphorus compounds, by the action of alcohols on the lower sulphides of phosphorus,[635] (*b*) from dialkyl phosphorochloridites by the action of hydrogen sulphide in the presence of a weak tertiary organic base such as pyridine,[609, 634] (*c*) from dialkyl *N,N*-diethylphosphoroamidites by the action of hydrogen sulphide,[596] and (*d*) by treating dialkyl phosphites with phosphorus pentasulphide.[608] Mixed ethyl alkyl hydrogen phosphonothionates have been prepared by transesterification of diethyl hydrogen phosphonothionate with higher alcohols, using phosphoric acid as catalyst[1101]:

$$
\begin{gathered}
P_4S_6 + ROH \rightarrow (RO)_2PS.H \\
(RO)_2P{-}Cl + H_2S \xrightarrow{\text{base}} B,HCl + (RO)_2PS.H \\
(RO)_2PNEt_2 + H_2S \rightarrow (RO)_2PS.H + Et_2NH \\
(RO)_2PO.H \xrightarrow{P_2S_5} (RO)_2PS.H \\
(EtO)_2PS.H + ROH \rightarrow RO(EtO)PS.H + EtOH
\end{gathered}
$$

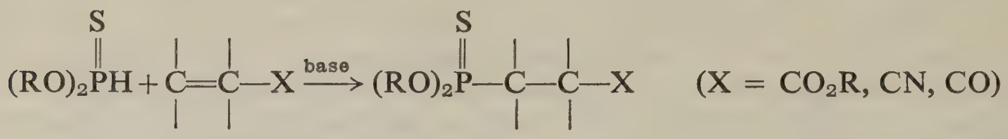
The lower dialkyl hydrogen phosphonothionates, unlike their oxygen analogues, are sparingly soluble in, and are not decomposed by, water.[609] However, in many respects the chemistry of the two classes of compound is similar and many of the typical reactions of dialkyl phosphites have been shown to take place with the phosphonothionates. Thus, chlorination with sulphuryl chloride[569] or with carbon tetrachloride and a base[697, 1611] yields dialkyl phosphorochloridothionate; thiocyanogen forms a dialkyl phosphorothiocyanatothionate.[640] Dialkylamino sulphenyl chloride reacts to form a tetra-alkyl trithiopyrophosphate[1078, 1099–1100]:

$$(RO)_2PS.H + SO_2Cl_2 \rightarrow (RO)_2PS.Cl + HCl + SO_2$$

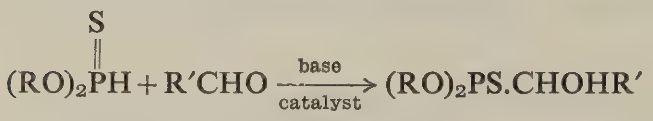
$$(RO)_2PSH + QSCl \rightarrow (RO)_2PS.SQ + HCl \rightarrow (RO)_2PS.SCl + QHCl \xrightarrow[\text{base, B}]{(RO)_2PSH} (RO)_4P_2S_3 + B,HCl$$

(Q = aliphatic, aromatic or heterocyclic secondary amine.)[1099]

In the presence of a base catalyst, hydrogen phosphonothionates add to the carbon–carbon double bond of many activated unsaturated compounds such as esters of maleic,[654] crotonic,[654] cinnamic,[654] acrylic,[654] and alkylidene malonic[695] acids and α-β unsaturated ketones and nitriles,[699] giving dialkyl β-substituted alkyl phosphonothionates. Similar addition takes place with the C=N double bond in anils.[1101] Aldehydes, ketones and α-β unsaturated aldehydes react to form dialkyl α-hydroxyalkyl phosphonothionates[639, 699]; in the presence of ammonia the product is a dialkyl α-aminoalkyl phosphonothionate:



$$(RO)_2\overset{S}{\overset{\|}{P}}H + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{base}} (RO)_2\overset{S}{\overset{\|}{P}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \qquad (X = CO_2R,\ CN,\ CO)$$

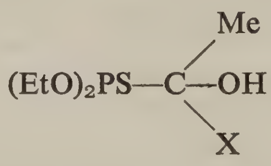


$$(RO)_2\overset{S}{\overset{\|}{P}}H + R'CHO \xrightarrow[\text{catalyst}]{\text{base}} (RO)_2PS.CHOHR'$$

An interesting difference between dialkyl phosphites and dialkyl hydrogen phosphonothionates is found in the reaction with chloral; the phosphite gives the expected 1-hydroxy-2,2,2-trichloroethyl phosphonate but the phosphonothionate product loses hydrogen chloride and rearranges to yield a dialkyl β,β-dichlorovinyl phosphorothiolate[609, 1098]:

$$(RO)_2PO.H + CCl_3CHO \rightarrow (RO)_2PO.CHOHCCl_3$$
$$(RO)_2PS.H + CCl_3CHO \rightarrow (RO)_2PS.OCH{=}CCl_2 \rightarrow (RO)_2PO.SCH{=}CCl_2$$

Carbonyl compounds of the type $CH_3COX$ ($X = PO(OEt)_2$, $CO_2Et$, $COCH_3$, Ph) react exothermically with diethyl thiophosphites in the absence of catalyst to form



If heated in the presence of sodium alkoxide, the compounds where X is $(EtO)_2PO$, $CO_2Et$ or $COCH_3$, undergo rearrangement to phosphates or phosphorothiolates, while the compounds where X = Ph are cleaved to $(EtO)_2PSH$ and $PhCOCH_3$.[1698]

Alkali-metal salts of dialkyl phosphorothionites are less soluble in organic media such as toluene than the corresponding salts of dialkyl phosphites.[697] Sodium diethyl thiophosphite is stated by Pudovik and Tarasova to decompose at 100°–110° giving triethyl phosphite and disodium *O*-ethyl phosphorodithioite[1692]:

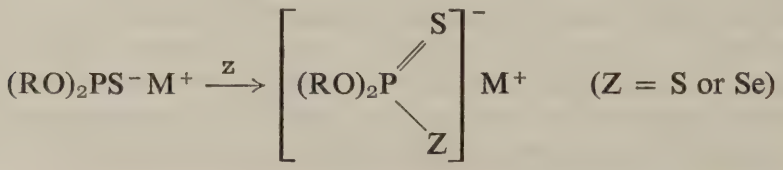
$$2\,(EtO)_2PSNa \xrightarrow{100\text{–}110^\circ} (EtO)_3P + EtOP(SNa)_2$$

The same workers report the following decomposition for sodium diethyl phosphite:

$$(EtO)_2PONa \xrightarrow{\Delta} (EtO)_3P(\text{trace}) + EtPO(OEt)_2 + EtPO(ONa)_2$$

Although the esters themselves are weak nucleophiles the sodium and potassium salts are strongly nucleophilic[634] and also exhibit the typically unsaturated character of trivalent phosphorus compounds. They react rapidly with alkyl halides giving dialkyl alkylphosphonothionates,[696, 768] with acyl halides giving dialkyl acylphosphonothionates, and readily add sulphur or selenium forming the corresponding dithio or selenothiophosphate[610, 636]:

$$(RO)_2PS^-M^+ \xrightarrow{R'X} R'PS.(OR)_2 + MX \qquad (X = \text{halogen})$$



### Dialkyl Hydrogen Phosphonoselenoates (dialkyl selenophosphites) $(RO)_2PSe.H$

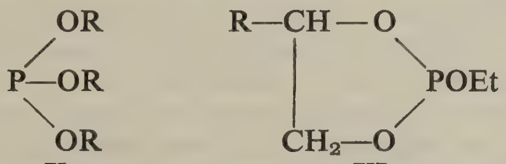
These compounds have been obtained by the action of hydrogen selenide on dialkyl phosphorochloridites in the presence of a tertiary organic base[769]:

$$(RO)_2PCl + H_2Se + R_3N \rightarrow (RO)_2PSe.H + R_3N.HCl$$

They react vigorously with sulphuryl chloride forming dialkyl phosphorochloridoselenoates, and undergo base-catalyzed addition to acrylonitrite giving dialkyl 2-cyanoethyl phosphonoselenoates.[769]

### Phosphorous Acid Triesters, $(RO)_3P$

Trialkyl phosphites are colourless liquids which are fairly readily oxidized by atmospheric oxygen. The lower members, particularly trimethyl phosphite, possess an unpleasant carbylamine-type odour. The lower members are soluble in, and are slowly hydrolyzed by, water; solubility and rate of hydrolysis decrease with increasing molecular weight. The hydrolysis is retarded by bases[770] and is strongly accelerated by acids.[781, 861] In pure water the hydrolysis is mildly catalyzed by dialkyl hydrogen phosphite, the first product of hydrolysis.[770] Hydrolysis of trialkyl phosphites derived from optically active alcohols shows that both acid- and base-catalyzed reaction involves P–O bond fission.[784] Phosphites in which the phosphorus atom forms part of a 1,3-dioxalane ring (XI) are rapidly hydrolyzed by water. When R = H, ring fission occurs leading to ethyl 2-hydroxyethyl hydrogen phosphite, but when R = –OEt, –CH$_2$OEt or –CH$_2$Cl, the ring is preserved and a substituted ethylene hydrogen phosphonate results[781]:



X XI

In contrast to trialkyl phosphites the rate of hydrolysis of triphenyl phosphite is accelerated by bases.[770]

The spectra of trialkyl phosphites indicate the structure X.[613] The relationship between parachor and structure in trialkyl phosphites, trialkyl phosphates, and trialkyl phosphorothionates, has been investigated by Arbuzov and Vinogradova.[771–3] They conclude that the phosphates carry all three alkyl chains in parallel positions, whereas in trialkyl phosphites only two of the alkyl chains are parallel. Heats of mixing of di- and tri-alkyl phosphites with chloroform are given by Kosolapoff.[774] Surface-tension values, determined by the method of maximum bubble pressure,[772] and dipole moments determined from dielectric constant measurements in carbon tetrachloride[776] are given by Arbuzov and co-workers. Atomic refractivities of phosphorus, oxygen and chlorine, in trialkyl phosphites and phosphorochloridites and in the corresponding phosphates and phosphorochloridates are given by Kabachnik *et al.*[777, 779] Bond and molar refractions of a large number of organophosphorus compounds are given by Sayre.[778]

The heats of formation of trimethyl phosphite and triethyl phosphite have been derived from the heats of esterification of phosphorus trichloride by methyl alcohol and ethyl alcohol in *cyclo*hexane solution.[780] They are:

$$\Delta H_f^\circ\,[P(OMe)_3, \text{liq.}] = -175{\cdot}0 \text{ kcal./mole}$$

and

$$\Delta H_f^\circ\,[P(OEt)_3, \text{liq.}] = -204{\cdot}1 \text{ kcal./mole}$$

The mean bond dissociation energies $\bar{D}$(P–OR) were calculated to lie within the range 79–82 kcal./mole. Mass spectra of trialkyl phosphites and dialkyl hydrogen phosphites have been recorded[782] and related to their radiolytic decomposition in the liquid phase.[783]

### PREPARATION

Although the reaction of phosphorus trihalides with sodium alkoxides formed the basis of the classical work by Arbuzov[820, 904] on the preparation of trialkyl phosphites, this method is rarely used today owing to the formation of by-products.[1, 813] Use of magnesium alkoxides in place of sodium alkoxides gives poor yields of trialkyl phosphites.[788]

The most general and widely used method of preparing trialkyl phosphites is by interaction of a phosphorus trihalide, usually the trichloride, with a hydroxy-compound or a mercaptan[1, 237, 848] in the presence of three equivalents of a tertiary organic base, B. Unsymmetrical tertiary phosphites[813, 819, 844] and mixed oxygen-sulphur esters[853] may be obtained using a phosphorochloridite or phosphorodichloridite in place of phosphorus trichloride:

$$3ROH + PCl_3 + 3B \rightarrow (RO)_3P + 3B,HCl$$

In its normal form the reaction is conducted by adding phosphorus trichloride to a stirred, cooled solution of a slight excess of the hydroxy-compound in an inert solvent such as benzene, petroleum ether or methylene dichloride and tertiary amine at 10°–15°. The product is filtered to remove base hydrochloride and the solution distilled under reduced pressure to obtain the phosphite. Bases such as pyridine, tributylamine, dimethylaniline or diethylaniline, have been used.[1, 785, 786, 812, 815, 817]

Industrially, the preparation of trialkyl phosphites is generally conducted using ammonia as the neutralizing base rather than an organic amine. Methods have been described in which the reaction of phosphorus trichloride and alcohol is conducted in a solvent at a temperature which is sufficiently low (−25°C.) to prevent dealkylation by hydrogen chloride, followed by neutralization at −25° with dry ammonia[787]; the simultaneous reaction of phosphorus trichloride and alcohol with a balanced stream of ammonia so as to maintain the pH of the mixture at 7–8·5, using a visual indicator such as methyl red, has also been described.[814, 818] Use of ammonium carbamate as neutralizing base is also suggested.[816]

Triaryl phosphites are not dearylated by hydrogen chloride and are prepared by reaction of phosphorus trichloride with a slight excess of a phenol at somewhat elevated temperatures.[821–3] Phenols of higher molecular weight usually react satisfactorily in the presence of a catalytic amount of magnesium chloride.[823] No product other than triaryl phosphite is formed in the reaction. Trialkyl and triaryl phosphorotrithiolites are similarly prepared[1]; the reaction is catalyzed by pyridine hydrochloride. The phosphites derived from certain strongly electronegatively substituted alcohols are not dealkylated by hydrogen chloride and may be prepared in the absence of bases; examples are: $CH_3CHCN.OH$,[804] $(CH_3)_2CCN.OH$,[879] $CCl_3.CH_2OH$,[799] and $CF_3CH_2OH$.[1481] The hydroxyl group in 1,1,1,3,3,3-hexachloropropane-2-ol is so deactivated that it does not react with phosphorus trichloride except in the presence of pyridine, when it yields the tertiary phosphite.[798]

### *Transesterification*

Trialkyl phosphites undergo an uncatalyzed exchange reaction when heated with aliphatic alcohols to yield mixtures of tertiary phosphites containing different alkyl groups; the relative amounts of these are determined by the proportion of reagents used[800]:

$$R'OH + (RO)_3P \rightleftharpoons R'OP(OR)_2 + ROH$$
$$R'OH + R'OP(OR)_2 \rightleftharpoons (R'O)_2POR + ROH$$

The transesterifications are catalyzed by bases, e.g. sodium alkoxide, and less efficiently by acids such as phosphoric acid. Difficulty is experienced in the isolation of the products if the boiling points of the exchanging and exchanged alcohol are too close[845]; use of trimethyl phosphite with higher alcohols gives good yields of the higher trialkyl phosphite[876]:

$$(MeO)_3P + 3ROH \xrightarrow{\text{base}} (RO)_3P + 3MeOH$$

Transesterification of triaryl phosphites with aliphatic alcohols has been used to prepare mixed alkyl-aryl phosphites[803, 813, 819, 871] and trialkyl phosphites. Since the displaced phenol may be reconverted to triaryl phosphite by direct reaction with phosphorus trichloride, this method provides a route to the trialkyl phosphites which avoids the use of an organic base or ammonia. Three methods have been described: (*a*) use of a high-boiling alcohol[803] or mercaptan[846] using base[846] or diphenyl phosphite[1701] as catalyst and removal of the phenol by distillation under vacuum, (*b*) use of a low-boiling alcohol such as methanol and fractionation of the trimethyl phosphite from the phenol,[801] and (*c*) treating triphenyl phosphite with 6–9 moles of an alcohol and sufficient sodium or potassium hydroxide to convert all the phenol to metal phenoxide, which is then removed by water washing.[802] For example,

$$(a)\ (PhO)_3P + C_{12}H_{25}SH \xrightarrow{\text{NaOPh}} (PhO)_2PSC_{12}H_{25} \rightarrow PhOP(SC_{12}H_{25})_2 \rightarrow P(SC_{12}H_{25})_3$$

$$(b)\ (PhO)_3P + CH_3OH(\text{excess}) \xrightarrow{\text{NaOPh}} (CH_3O)_3P\uparrow + 3PhOH$$

$$(c)\ (PhO)_3P + CH_2{=}CH{-}CH_2OH + 3NaOH \rightarrow (CH_2{=}CH{-}CH_2O)_3P + 3NaOPh + 3H_2O$$

The transesterification of trivalent phosphorous esters has been reviewed by Petrov *et al.*[2398]

### *Miscellaneous Methods*

Trialkyl phosphites have been prepared by interaction of phosphorus trichloride with alkali-metal salts of alkyl carbonic acids; possibly there are formed intermediate substances such as $(ROCO_2)_3P$ which lose carbon dioxide giving the product.[806] Butoxytrimethyl silane undergoes an exchange reaction with phosphorus trichloride in the presence of a catalytic amount of pyridine hydrochloride[805]:

$$3Me_3SiOBu + PCl_3 \xrightarrow{C_5H_5N.HCl} (BuO)_3P + 3Me_3SiCl\uparrow$$

The reaction of tetraethyl silicate with phosphorus trichloride gives ethyl phosphorodichloridite and diethyl phosphorochloridite but no triethyl phosphite.[807] Ethyl orthopropionate and phosphorus trichloride react to give a mixture of triethyl phosphite and diethyl-1,1-diethoxypropylphosphonate.[807]

Good yields of trialkyl phosphites,[808] alkyl arylphosphites,[570] alkyl and aryl trithiophosphites[570] and diesters of phosphonous and phosphonodithious acids[570] are obtained by reaction of the appropriate dialkyl amides of trivalent phosphorous acids with alcohol, phenol, or mercaptan:

$$P(NMe_2)_3 + 3ROH \rightarrow P(OR)_3 + 3Me_2NH$$
$$RP(NEt_2)_2 + 4PhSH \rightarrow RP(SPh)_2 + 2PhSH,Et_2NH$$

Unsymmetrical phosphites are obtained by adding an alcohol or phenol to an acyl phosphite and triethylamine at room temperature[1702]:

$$(RO)_2P{-}OCOCH_3 + R'OH + Et_3N \rightarrow (RO)_2P{-}OR' + CH_3CO_2H,Et_3N$$

Trivinyl phosphite, mixed alkyl-vinyl phosphites, and divinyl phosphonites have been prepared from phosphorus trichloride, phosphorochloridite or phosphonous dichloride, respectively, by reaction with mercury, acetaldehyde, and triethylamine[789-90]:

$$PCl_3 + Hg(CH_2CHO)_2 \rightarrow P(OCH{=}CH_2)_3$$

Dialkyl phosphites are not further alkylated by diazoalkanes, but diphenyl phosphite and diazomethane react to form diphenyl methyl phosphite.[615] Reduction of trialkyl phosphorothionates with sodium affords the trialkyl phosphite[809]:

$$(RO)_3PS + 2Na \rightarrow (RO)_3P + Na_2S$$

Benzoic acid reacts with phosphorus trichloride and pyridine giving tribenzoyl phosphite, but aliphatic carboxylic acids are said to yield the acyl halide as primary product[811]:

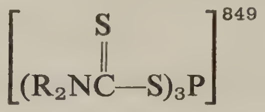
$$3PhCO_2H + PCl_3 + 3C_5H_5N \rightarrow (PhCOO)_3P + 3C_5H_5N{,}HCl$$

Organic disulphides react with white phosphorus at 200° giving trialkyl phosphorotrithioites[847,1189]:

$$6RSSR + P_4 \rightarrow 4(RS)_3P$$

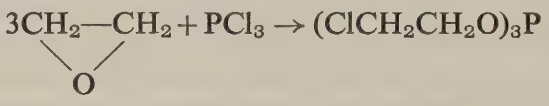
The same products are obtained in >90% yield by the reaction of white phosphorus and disulphides in the presence of strongly basic catalysts under mild conditions in aprotic solvents such as dimethyl formamide or dimethyl sulphoxide.[2062]

Dialkyl aminodithiocarbamates and phosphorus trichloride react to form tris(dialkylaminothiocarbamyl) phosphorotrithioites[849]:



$$\left[(R_2N\overset{\overset{\displaystyle S}{\|}}{C}{-}S)_3P\right]^{849}$$

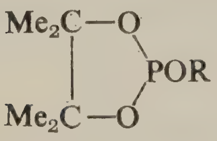
Phosphorus trichloride or tribromide reacts readily with alkylene oxides giving tris(2-halogenoalkyl) phosphites[834-5,1104]:



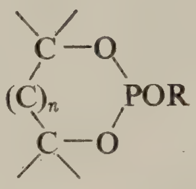
$$3\underbrace{CH_2{-}CH_2}_{O} + PCl_3 \rightarrow (ClCH_2CH_2O)_3P$$

Phosphine and trifluoromethyl sulphenyl chloride react to form a mixture of $(CF_3S)_2PH$ and $(CF_3S)_3P$.[1703]

Tertiary phosphites of numerous primary and substituted primary alcohols and phenols have been prepared.[1] Secondary alcohols generally give poorer yields. Phosphites of tertiary alcohols such as *tert*-butanol are difficult to prepare[593]; tri-*tert*-butyl phosphite[850-1] readily eliminates *iso*butylene on heating at 80°–90°. In contrast, the di-*tert*-alcohol, tetramethyl ethylene glycol, readily forms the cyclic phosphite **XII** on reaction with an alkyl phosphorochloridite and pyridine. A number of cyclic phosphites (2-alkoxy-1,3,2-dioxaphospholanes) **XIII**, have been prepared

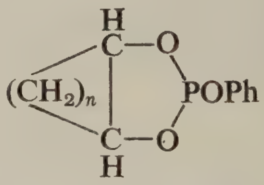


**XII**



*n* = 0, 1, 2

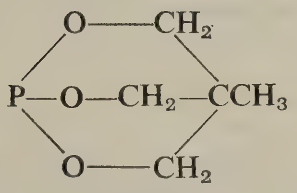
**XIII**

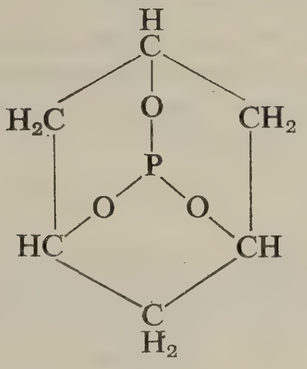


*n* = 3, 4

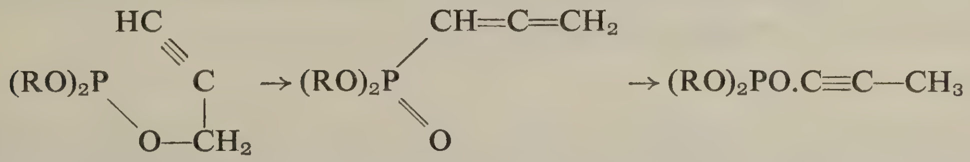
**XIV**

by Arbuzov and co-workers[781,796-7,828] from the corresponding cyclic phosphorochloridites (1-chloro-1,3,2-dioxaphospholanes). Similar compounds, R = Ph, *n* = 0,1,2,3, have been obtained by Rydon[871] by transesterification of aliphatic glycols with triphenyl phosphite; polymeric by-products which range from oils (from the lower glycols) to a rubber-like solid (with hexane-1,6-diol) are also formed. Compounds **XIV** result from transesterification with *cis-cyclo*pentane-1,2-diol and *cis-cyclo*hexane-1,2-diol. Other novel cyclic phosphites which have been prepared are 1-methyl-4-phospha-3,5,8-trioxabi*cyclo*(2,2,2)-octane[794] **XV**, and related compounds,[1108] and phospha-2,8,9-trioxa-adamantane **XVI**.[795,876,1102] Dipole moments of **XV** and **XVI** and their corresponding phosphates and thionophosphates are recorded.[876]

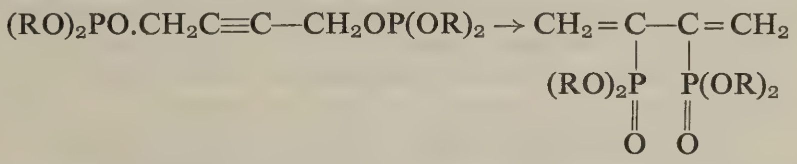

**XV**


**XVI**

Allyl and benzyl groups are readily removed from phosphorous esters by dealkylation with hydrogen chloride or amine hydrochlorides. Tribenzyl phosphite has not been described. Dialkyl alkynyl phosphites derived from primary α-acetylenic alcohols such as propargyl alcohol readily undergo rearrangement on heating, giving dialkyl 1,2-propadienylphosphonate and dialkyl 1-propynephosphonate[792,1103]:

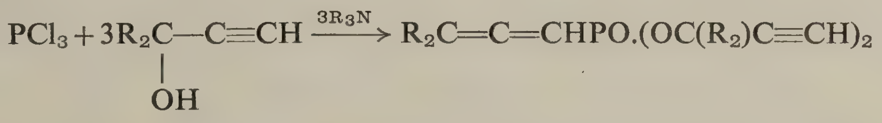


The tetra-alkyl diphosphite from butyne-1,4-diol rearranges exothermically at room temperature giving tetra-alkyl 2,3-diphosphonobutadiene[793]:

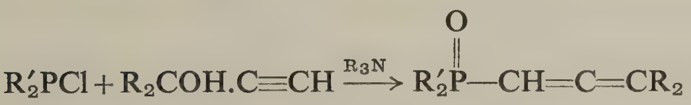


$$(RO)_2PO.CH_2C{\equiv}C{-}CH_2OP(OR)_2 \rightarrow CH_2{=}\underset{\underset{\displaystyle O}{\|}}{\underset{|}{\overset{}{C}}}\!\!\!\!\!\!\!\!\!\!\phantom{x}{-}C{=}CH_2 \quad [C_2: (RO)_2P(=O),\ C_3: P(=O)(OR)_2]$$

Tertiary α-acetylenic alcohols react with trivalent phosphorus compounds ($R_2PCl$, $RPCl_2$, $PCl_3$) in the presence of organic base giving allenic pentacovalent phosphorus compounds (phosphine oxide, phosphinate ester, phosphonate ester, respectively)[791]:



$$PCl_3 + 3R_2\underset{\underset{\displaystyle OH}{|}}{C}{-}C{\equiv}CH \xrightarrow{3R_3N} R_2C{=}C{=}CHPO.(OC(R_2)C{\equiv}CH)_2$$



$$R_2'PCl + R_2COH.C{\equiv}CH \xrightarrow{R_3N} R_2'\overset{\overset{\displaystyle O}{\|}}{P}{-}CH{=}C{=}CR_2$$

### REACTIONS OF TERTIARY PHOSPHITES

#### *Complex Formation*

Trialkyl and triaryl phosphites combine with many metal halides and pseudo halides to give co-ordination complexes which are frequently crystalline and have characteristic melting points. Complexes of the following types have been described {L = $(RO)_3P$ or $(PhO)_3P$}: L,CuX (X = Cl, Br, I, CNS[400, 855] and CN[854]); 2L,CuX (X = Cl, Br, I,[855] CN[854]); LL′,CuX (where L = $(PhO)_3P$, L′ = $(RO)_3P$, $C_5H_5N$ or $Ph_3As$, X = halogen)[940]; L,AgX (X = Cl, Br, I)[855]; L,AuCl[855]; L,$PtCl_2$[855]; L,$(HgCl_2)_2$[855]; L,$HgX_2$ (X = Cl, Br, I)[855]; $L_4$Pt,$PtCl_2$[857, 861]; $L_4$,M (where L = $(EtO)_3P$, M = Co, Ni).[810, 2405] In many cases the same complexes can be synthesized by reacting an alcohol or phenol with the appropriate complex of phosphorus trichloride with the metal halide.[855, 859] Cryoscopic molecular weight determinations on a number of complexes have been carried out by Arbuzov.[855]

The complex of trimethyl phosphite and cuprous chloride, $(MeO)_3P,CuCl$, which may be prepared from the phosphite directly or by methanolysis of the $PCl_3,CuCl$ complex, undergoes isomerization and decomposition at 200°, giving dimethyl methyl phosphonate[928]:

$$(MeO)_3P,CuCl \xrightarrow[\text{Dowtherm}]{200^\circ \text{ in}} MePO(OMe)_2$$

The preparation of complexes of trialkyl phosphite and borine has been investigated by Reetz and Katlafsky.[858] They found the trialkyl phosphites to be strong Lewis bases (in the case of tri-*iso*propyl phosphite, of the same strength as trimethylamine). The complexes may be obtained by the reaction:

$$NaBH_4 + CO_2 + P(OR)_3 \rightarrow NaOCHO + (RO)_3P,BH_3$$

The relative stability order of borine co-ordination complexes with various trivalent phosphorus compounds is given as[860]:

$$PCl_3 < PH_3 < PF_3 < PR_3 < P(OR)_3 < P(NR_2)_3$$

Trialkyl phosphites give no colour with carbon disulphide, thus differing in this respect from phosphonous diesters which give red solutions and from tertiary phosphines which form red crystalline adducts.[411]

### *Oxidation*

Although direct oxidation by oxygen to corresponding phosphates has been reported for certain specific tertiary phosphites such as tris-1-cyano-*iso*propyl,[879] tris-*p*-chlorophenyl,[880] and triallyl phosphites,[1188] this method fails with triethyl phosphite[872] and is of little practical value for the preparation of phosphates. Photochemically induced oxidation of a variety of trialkyl phosphites is reported to proceed readily[867, 1190] but with trimethyl and triaryl phosphites the oxidation is unsatisfactory.[1190] Unsaturated tertiary phosphites are reported to be oxidized by air in the presence of alumina catalyst[1704]; trithiophosphites can be oxidized by air at 110°C. to about 80% completion and then by hydrogen peroxide to about 95% completion.[1124] Methods involving "wet" oxidation are generally not satisfactory owing to extensive hydrolysis of the phosphite. Reagents which have been used successfully to oxidize tertiary phosphites are ozone,[865–6] sulphur dioxide with phosphorus tribromide as catalyst,[1681] sulphur trioxide in liquid sulphur dioxide solution,[874] sulphur trioxide alone,[1494] aqueous hydrogen peroxide in slightly alkaline solution,[864] nitrogen tetroxide,[872] nitrous oxide,[873] manganese dioxide,[871] mercuric oxide,[870, 871] lead tetraacetate,[889] aqueous chloramine *T*,[637] organic peroxides,[881] and hydroperoxides,[118, 881, 875] peracids such as perbenzoic acid, and *tert*-butyl hypochlorite.[114]

Complexes of the type $(ArO)_3P,O_3$ have been described by Thompson[866] as intermediates in the oxidation of triaryl phosphites by ozone. The products isolated from reaction of tertiary phosphites and dialkyl peroxides are consistent with a free-radical reaction mechanism which involves the formation of an intermediate phosphoranyl radical by the addition of alkoxy-radical to the phosphite (cf. the review 'Radical Reactions of Organophosphorus Compounds'[2314]):

$$RO\cdot + (RO_3)P \rightarrow (RO)_3\dot{P}{-}OR \xrightarrow{\text{fast}} (RO)_3PO + R\cdot$$

The reaction with alkyl hydroperoxides giving phosphate and alcohol has been formulated as an ionic process.[875, 881]

Trialkyl phosphites are excellent deoxygenating reagents,[355] the phosphite itself being oxidized to phosphate. Examples of some compounds which are reduced by trialkyl phosphites are given below:

epoxides → olefins[883]
isocyanates → isonitriles[884]
phthalic anhydride → biphthalyl[885-6]
pyridine *N*-oxide → pyridine[355, 887-8]
diaryloyl peroxides → diaryloyl esters[869]
nitrosobenzene → azoxybenzene[868]
hydroperoxides → alcohols
*O*-nitrostyrenes → 2-substituted indoles[2055]

*Formation of Thiono- and Selenono-phosphates*

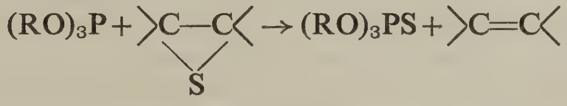
Trialkyl phosphorothionates are readily formed by the addition of sulphur to trialkyl phosphites[1, 399, 1289, 771]; selenium adds less readily to give the phosphoroselenonate:

$$(RO)_3P + S \text{ or } Se \rightarrow (RO)_3PS \text{ or } (RO)_3PSe$$

Triaryl phosphites and aryl phosphorochloridites readily desulphurize $PSCl_3$[1184]:

$$(PhO)_3P + PSCl_3 \rightarrow (PhO)_3PS + PCl_3$$
$$PhOPCl_2 + PSCl_3 \rightarrow PhOPSCl_2 + PCl_3$$

Phosphorothionates also result from reaction with an episulphide,[127, 890] the episulphide being reduced stereospecifically to the corresponding olefin[126, 893]:



Under the influence of free-radical initiators alkane thiols react with trialkyl phosphite yielding the trialkyl phosphorothionate and a hydrocarbon.[881, 894] Rabinowitz and Walling[881, 895] conclude that direct attack of thiyl radicals on phosphorus occurs giving an intermediate tetravalent phosphoranyl radical $(RO)_3\dot{P}\text{–}SR'$ which subsequently breaks down with C–S bond fission to phosphorothionate and an alkyl radical which can perpetuate a chain-reaction:

$$RS\cdot + (RO)_3P \rightarrow (RO)_3\dot{P}\text{—}SR \rightarrow (RO)_3P{=}S + R\cdot$$
$$R\cdot + RSH \rightarrow RH + RS\cdot$$

Dialkyl disulphides react under free-radical conditions giving the thioether and phosphorothionate[881]; in contrast, at higher temperatures in the presence of free-radical inhibitors, reaction proceeds by an ionic Arbuzov-type reaction giving an *S*-alkyl dialkyl phosphorothioate and an unsymmetrical thioether.[896] The two modes of reaction are shown below.

$$(RO)_3PS + R'SR' \xleftarrow[R'S-SR']{\text{radical catalyst}} (RO)_3P \xrightarrow[R'S-SR']{\text{heat}} (RO)_2PO.SR' + RSR'$$

Diacyl disulphides such as diacetyl disulphide,[1004] dibenzoyl disulphide[896] and bis(diethoxyphosphinyl) disulphide react with trialkyl phosphite giving trialkyl phosphorothionate and diacylsulphide. Thiocyanogen behaves similarly.[1004] A modified Arbuzov reaction has been suggested[896, 1004]:

$$(RO)_3P + XSSX \rightarrow [(RO)_3P\text{—}S\text{—}X]^+SX^- \rightarrow (RO)_3PS + X_2S$$
$$(X = CH_3CO,\ PhCO,\ (EtO)_2PO,\ CN)$$

*Reaction with Halogens*

Dialkyl phosphorochloridates may be readily prepared by passing dry chlorine into ice-cold trialkyl phosphite.[700] Other reagents which may be used are sulphuryl chloride,[897] phosgene,[1127] and oxalyl chloride[901]:

$$(RO)_3P \xrightarrow[(COCl)_2,\ COCl_2]{Cl_2,\ SO_2Cl_2} (RO)_2PO.Cl$$

The reported formation of compounds of the type $(RO)_2PO.COCl$ and $[(RO)_2PO]CO$ by reaction of dialkyl phosphite and phosgene[1026] has been questioned by Petrov *et al.*[1634] Reaction with bromine gives the less stable dialkyl phosphorobromidates.[706, 902] Very unstable dialkyl phosphoroiodidates have been obtained in ethereal solution by the action of iodine on ice-cold phosphite.[700]

Sulphur monochloride[898] and sulphur dichloride[899] react with trialkyl phosphites forming both dialkyl phosphorochloridite and trialkyl phosphorothionate, and with triaryl phosphites to give triaryl phosphorothionate and triaryl phosphite dichlorides[900]:

$$S_2Cl_2 + 3(RO)_3P \rightarrow 2(RO)_3PS + RCl + (RO)_2PO.Cl$$
$$SCl_2 + 2(RO)_3P \rightarrow (RO)_3PS + RCl + (RO)_2PO.Cl$$

The reaction between triaryl phosphites and halogens (Cl, Br, I) has been clarified by the work of Rydon and Tonge.[924] The reaction of triphenyl phosphite with halogens proceeds in several stages, the first two of which are[924-5]:

$$2(PhO)_3P + X_2 \rightarrow (PhO)_2PX + (PhO)_4PX \qquad (X = Cl, Br, I)$$
$$(PhO)_2PX + (PhO)_4PX + X_2 \rightarrow 2(PhO)_3PX_2$$

Exchange of cation and anion amongst the dimeric forms of triphenoxyphosphorus dihalides can lead to the formation of all or any of the possible phenoxy-halides $(PhO)_nPX_{(5-n)}$. From a study of the alcoholysis and hydrolysis of these compounds, prepared either by addition of halogen to the phosphite or by the action of phosphorus pentachloride on phenol, it was concluded that the chloro- and bromo-compounds are dimeric polyhalogenopolyphenoxyphosphonium polyphenoxypolychlorophosphates, $[(PhO)_xPX_{(4-x)}]^+[(PhO)_yPX_{(6-y)}]^-$, or mixtures of such compounds, whereas the iodides are monomeric phosphonium compounds

$$[(PhO)_nPI_{(4-n)}]^+I^-$$

Triphenyl phosphite dihalides have been used as reagents for the preparation of alkyl halides[984]:

$$(PhO)_3PX_2 + ROH \rightarrow (PhO)_3PO + RX + HX$$

Triphenyl phosphite polyiodides $(PhO)_3PI^+I_n^-$ have been reported by Forsman and Lipkin.[1005] Reaction of triphenyl phosphite with ammonia and iodine gives $[PhO)_3P{-}N{=}P(OPh)_3]^+I^-$.[1005]

*The Michaelis–Arbuzov Reaction*

One of the classical phenomena of organophosphorus chemistry is the reaction, discovered by Michaelis and Kaehne[903] and developed by Arbuzov,[904] in which a trialkyl phosphite is heated with an alkyl halide to form a dialkyl alkylphosphonate and a new molecule of alkyl halide.[1, 911] In its simplest form, interaction of *n*-alkyl halide with a tri-*n*-alkyl phosphite, the reaction may be written:

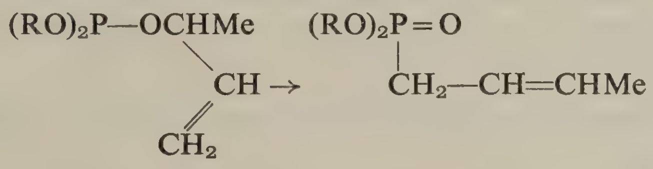
$$R'X + (RO)_3P \rightarrow [(RO)_3\overset{+}{P}{-}R']X^- \rightarrow (RO)_2PO.R' + RX$$

The reaction is generally believed to proceed by two consecutive bimolecular nucleophilic displacement reactions. In the first, trivalent phosphorus attacks the alkyl halide with fission of the C–X bond to form an alkyl trialkoxyphosphonium halide; in the second, the halide ion attacks one of the alkoxy-groups of the intermediate phosphonium salt.[717,896,905,907–10,918] The general observation that, with respect to alkyl halide, the reaction rate decreases in the order RI > RBr > RCl, and primary halide > secondary halide, and the low reactivity of *cyclo*hexyl *p*-toluenesulphonate with triethyl phosphite have been advanced in support of the mechanism of the first stage of reaction.[717,905] Overall reaction rates have been measured by a number of workers.[912–5,936–7,1109] Reaction of tris-2-octyl phosphite from optically active 2-octanol with ethyl bromide or with acetyl chloride gives optically inverted 2-bromo-octane and 2-chloro-octane, respectively, indicating the $S_N2$ character of the second reaction step.[905]

Physico-chemical evidence for the existence of the intermediate quasiphosphonium salts has been advanced by Arbuzov and co-workers[917–8,933] and by Abramov,[919,923,926] and is strongly supported by the isolation of salt-like quasiphosphonium halides from the reaction of triaryl phosphite,[903,916] diesters of phosphonous acids,[421,920,1723] and esters of phosphinous acids[421,2387–8] with alkyl halides and by the formation of quasiphosphonium fluoroborates from the reaction of trialkyl phosphites with carbonium-ion tetrafluoroborates.[921–2]

No exchange of radio-active phosphorus takes place between triethyl phosphite and diethyl ethyl phosphonate indicating that the reaction is irreversible.[927]

Trialkyl phosphites have been isomerized to the corresponding alkyl dialkyl phosphonates by heating at 250° without catalyst[1105] and at lower temperatures by the Arbuzov reaction using catalytic amounts of reagents such as methyl iodide,[813,931] dimethyl sulphate,[813] ethyl toluene sulphonate[717] or sodium iodide.[929] Diphenyl alkylphosphonates are formed by heating $(PhO)_3P$, an alcohol, and a catalytic amount of sodium iodide.[930] Allyl dialkyl phosphites undergo a Claisen-type rearrangement on heating, giving 2-propenyl phosphonates[932]:



Phosphites which contain halogenoalkyl substituents readily undergo isomerization on being heated; thus tris-2-chloroethyl phosphite rearranges to bis-(2-chloroethyl) 2-chloroethyl phosphonate.[934]

### *Scope of the Arbuzov Reaction*

(*a*) The phosphorus component

The Arbuzov reaction occurs between a wide range of trivalent phosphorous esters and alkyl halides. The following classes of esters participate: mixed trialkyl phosphites,[844] trialkyl phosphorothionites and dithionites,[853,1595] aryl dialkyl and diaryl alkyl phosphites,[914] vinyl dialkyl and divinyl alkyl phosphites,[789–90] dialkyl phosphoramidites[863,1595,878,941–2,1087] and alkyl phosphorodiamidites,[943,946,2406] diesters of phosphonous[415–8,840] and phosphonodithious acids,[945] esters of phosphinous[526,920] and phosphinothious acid,[944] and esters of pyrophosphorous acid.

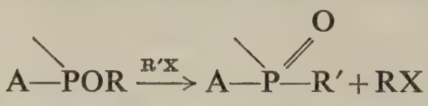
In a number of these reactions moderately stable intermediate quasiphosphonium salts have been isolated.[421,920,941,943,945,1723]

The effects of substituents attached to the phosphorus atom on the reaction rate are generally in accordance with the predicted electron-donating or electron-attracting effect of the substituent on the electron density at the phosphorus atom. Thus, the reaction rate increases in the series:

$$ArOP(OAlk)_2 < AlkOP(OAlk)_2 < AlkP(OAlk)_2$$

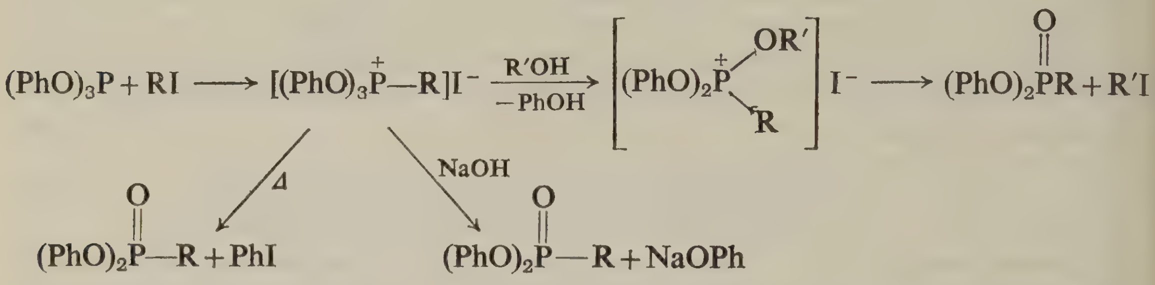
In the series of compounds $(EtO)_3P$, $EtP(OEt)_2$, $Et_2POEt$, the relative reaction times with ethyl iodide are 1214 : 12 : 1.[915]

In mixed trialkyl phosphites the smallest alkyl group is eliminated as alkyl halide,[844] in mixed phenyl alkyl phosphites, vinyl alkyl phosphites and alkyl phosphoroamidites the alkyl group is always eliminated:



$$\text{A—POR} \xrightarrow{\text{R}'\text{X}} \text{A—}\overset{\text{O}}{\text{P}}\text{—R}' + \text{RX} \qquad (\text{A} = \text{phenyl, vinyl, R}_2\text{N})$$

Triaryl phosphites, trivinyl phosphites, and trialkyl trithiophosphites do not undergo the Arbuzov reaction. Triaryl phosphites form moderately stable quasi-phosphonium salts which may be converted to diaryl alkylphosphonates by treatment with an alcohol[813] or with aqueous alkali or by heating at 200°[914]:



Diphenyl phenylphosphonite and phenyl diphenylphosphinite behave similarly.[421] The first reaction sequence above has been developed by Rydon[813] as a convenient route for the preparation of alkyl halides.

Trivinyl phosphite decomposes on being heated with methyl iodide at 120°.[790] Trithiophosphites form crystalline adducts with alkyl halides[852] and these adducts were shown by Divinskiĭ, Kabachnik and Sidorenko[947] to be the products of alkylation at a sulphur atom. The adducts decompose on heating giving dialkyl dithiophosphorous halides (*S,S*-dialkyl phosphorohalidodithioites):

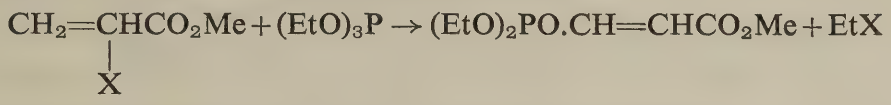
$$(\text{RS})_3\text{P} + \text{RX} \rightarrow (\text{RS})_2\text{P—}\overset{+}{\text{S}}\text{R}_2\text{X}^- \xrightarrow{\Delta} (\text{RS})_2\text{PX} + \text{RSR}$$

### (*b*) The alkyl halide

Trialkyl phosphites undergo the Arbuzov reaction with a wide range of alkyl halides to form the corresponding phosphonic acid esters.[1, 2] The phosphonic esters have been thus obtained in good yield from the following halogen compounds: low molecular-weight and long-chain primary alkyl halides[948, 715]; arylalkyl halides such as benzyl halides and their nuclear substituted derivatives[958, 973, 1085]; halogenomethyl naphthalene and halogenomethyl substituted heterocyclic compounds [1111]; halogenomethyl ethers such as chloromethyl benzyl ether[949]; $\omega$-halogeno esters[2406] such as $\beta$-bromopropionic ester[983]; $\omega$-bromoundecanoates[961]; $\omega$-halogen substituted quaternary ammonium compounds[968]; halogenohydrins such as epibromohydrin[656]; and chloromethyl cyanide.[1722] The reaction proceeds less well with secondary alkyl halides and generally good yields of phosphonate are obtained only with secondary halides which also carry an $\alpha$-activating group such as $\alpha$-bromo fatty acid esters,[721, 954, 962–3] $\alpha$-halogenoacetamide,[460, 960] diesters of $\alpha$-halogenomethylphosphonic acid,[745] bromoacetal[975] and chloroacetonitrile.[975] Diphenylmethyl bromide and 9-bromofluorene[964] react well; a free-radical reaction mechanism has been suggested for the reaction of these bulky halides.[964] Triarylmethyl halides form the expected triarylmethylphosphonates.

Aromatic halogen compounds do not undergo the Arbuzov reaction but a number of chlorosubstituted heterocyclic compounds such as 9-chloroacridine[1112] and 5-chloropyrimidine yield the expected phosphonates. In chlorotriazines the chlorine atom is replaced by the diethyl phosphono-group by reaction with triethyl phosphite[1086]; thus cyanuric chloride (2,4,6-trichlorotriazine) forms 2,4,6-tris-diethyl phosphonotriazine.[966] Cyanogen chloride or bromide and tertiary alkyl phosphites form dialkyl cyanophosphonates.[967, 1721]

Compounds having halogen attached to a carbon–carbon double bond react with difficulty. α-Halogenoacrylic esters and triethyl phosphite react with rearrangement giving diethyl 2-(carboxymethyl)vinylphosphonate[959]:

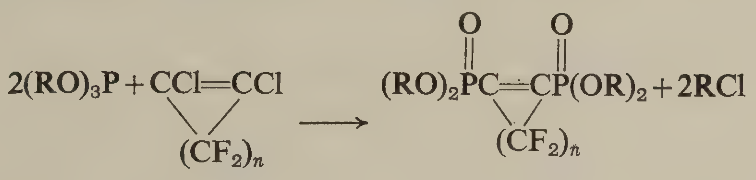


$$CH_2{=}\underset{\displaystyle X}{\underset{|}{C}}HCO_2Me + (EtO)_3P \rightarrow (EtO)_2PO.CH{=}CHCO_2Me + EtX$$

Perfluorovinylphosphonates have been obtained by the reaction of trialkyl phosphite with perfluoro*cyclo*butene, perfluoro*iso*butylene, and perfluoropropylene[971]:

$$(EtO)_3P + (CF_3)_2C{=}CF_2 \rightarrow (CF_3)_2C{=}CF{-}PO.(OEt)_2 + EtF$$

1,2-Dichloroperfluoro*cyclo*alkenes react with triethyl phosphite with displacement of both chlorine atoms to give tetra-alkyl perfluoro-1-*cyclo*alkene-1,2-diphosphonates.[2065] In contrast, saturated chlorofluorohydrocarbons react anomalously to give olefin and dialkyl phosphorofluoridate[2066]:

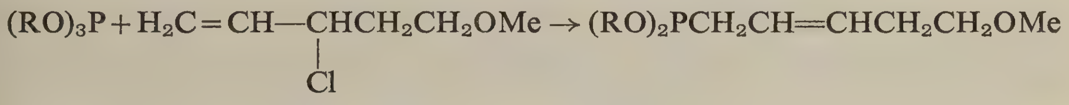


$$(RO)_3P + F(CF_2CFCl)_nF \longrightarrow F(CF{=}CF)_nF + (RO)_2POF + RCl$$

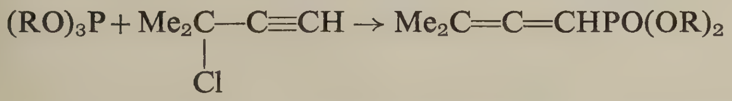
Aromatic imidoyl chlorides form the expected dialkyl phenyliminobenzyl phosphonates.[2408] Acetylenic halides such as phenyl chloroacetylene[715, 2407] and 1-bromo-3-butene-1-yne[1110, 957] form the corresponding alkynylphosphonates:

$$BrC{\equiv}C{-}CH{=}CH_2 + (RO)_3P \rightarrow (RO)_2PO.C{\equiv}C{-}CH{=}CH_2$$

Allyl halides and propargyl halides in which the halogen atom is attached to a primary carbon atom as in allyl chloride,[953] propargyl bromide[955] and 1-bromobut-2-yne[1110] form the expected phosphonate. When the halogen atom is attached to a secondary or tertiary carbon atom a rearranged product can result. Thus 3-chloro-1-methoxypent-4-ene gives 5-methoxy-pent-2-enyl phosphonate and 3-methyl-3-chlorobut-1-yne gives 3-methylbuta-1,2-dienyl phosphonate[956]:

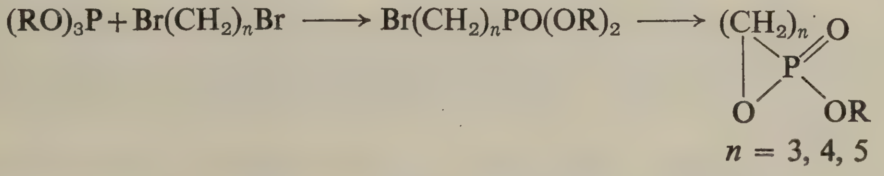


$$(RO)_3P + H_2C{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_2OMe \rightarrow (RO)_2PCH_2CH{=}CHCH_2CH_2OMe$$



$$(RO)_3P + Me_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}C{\equiv}CH \rightarrow Me_2C{=}C{=}CHPO(OR)_2$$

Compounds containing two primary halogen atoms such as α-ω dihalogenoalkanes[976] and bis-halogenomethyl ether[950] react with an excess of trialkyl phosphite giving good yields of the bis-phosphonate ester. With an excess of halogen compound ethylene dibromide forms a 2-bromoethyl phosphonate,[977] but with higher α-ω dibromides the initially formed ω-bromoalkyl phosphonate undergoes cyclization to form a phospholane derivative.[965] A similar alkylation has been demonstrated by Laughlin between dimethyl methylphosphonate and dodecyl bromide[952]:



$$MePO(OMe)_2 + C_{12}H_{25}Br \longrightarrow MePO(OMe)OC_{12}H_{25}$$

Methylene di-iodide and trialkyl phosphites react to form the dialkyl iodomethylphosphonate,[745] which can react with a further equivalent of trialkyl phosphite giving a tetra-alkyl methylenediphosphonate. Methylene dibromide reacts more slowly and it is necessary to conduct the reaction under pressure.[812] The reaction of methylene dichloride with trialkyl phosphites has not been reported.

Chloroform is reported not to react with triethyl phosphite even under vigorous conditions[364,458,980]; in the presence of benzoyl peroxide reaction occurs giving diethyl dichloromethylphosphonate. Carbon tetrachloride reacts with trialkyl phosphites at temperatures lower than those required for simple alkyl halides, giving high yields of trichloromethylphosphonates[844,979–80]; similarly trichlorofluoromethane gives $CFCl_2PO(OR)_2$.[1002] The reaction with carbon tetrachloride has been shown by Griffin[363] to proceed by a radical-chain process. Similar radical-chain processes have been suggested[982] for the reaction of trialkyl phosphites with trichlorobromomethane and carbon tetrabromide[1008] and for the benzoyl peroxide catalyzed reactions of dibromomethane, bromodichloromethane, bromochloromethane, and chloroform.[982] Support for the homolytic nature of the reaction of carbon tetrachloride with triethyl phosphite has been advanced by Cadogan.[355]

In some cases olefin formation occurs during the Arbuzov reaction. Formation of small amounts of olefin and dialkyl phosphite takes place when 1-halogenoalkanes having an activating group in the 2-position are reacted with trialkyl phosphite.[909] The preparative use of trialkyl phosphites as dehydrohalogenating agents has been described.[974] 3-Chloro*cyclo*pent-1-ene reacts with trialkyl phosphite to form *cyclo*pentadiene but with sodium diethyl phosphite giving the expected diethyl *cyclo*pent-2-enyl phosphonate.[969]

Dehalogenation occurs with certain polyhalogen compounds, e.g., phenanthrene-9,10-dibromide[720] and hexachloroethane[970] give phenanthrene and tetrachloroethylene respectively.

Chloro-urea and trialkyl phosphites react to form esters of ureido-phosphoric acid[2161]:

$$(RO)_3P + ClNHCONH_2 \rightarrow NH_2CONHPO(OR)_2 + RCl$$

*Reactions related to the Arbuzov Reaction*

A variety of compounds which contain polarized or easily polarizable linkages, which can undergo reaction with a nucleophile with displacement of an anion, will undergo reaction with trialkyl phosphite in an Arbuzov-type reaction:

$$(RO)_3P + A{-}X \rightarrow [(RO)_3\overset{+}{P}A]X^- \rightarrow (RO)_2PO.A + RX$$

Such reactions occur with molecular chlorine, bromine,[902] or iodine,[1005] alkyl sulphonate esters,[717] acyl halides,[508,725,745,990] carboxylic acid anhydrides,[997,1009] Mannich base salts,[985–6] *N*-alkyl[996] and *N*,*N*-dialkyl[995–6] carbamoyl chlorides and thiocarbamoyl chlorides,[998] sulphenyl[841,898,1003] and sulphonyl halides,[994,999] alkyl isothiocyanates and alkyl isoselenocyanates,[988] *N*,*N*-dialkylamino-sulphenyl chlorides,[1084] *N*-chloroamines,[993] *N*-chloro-benzamide and *N*-chloro-benzamidine,[1081] alkyl hypochlorites,[992] disulphides,[896,999] bis(dialkyloxythiophosphonyl) disulphides,[1605] alkyl alkanethiolsulphonates,[987] diselenides[1002] and bisdialkoxyphosphinyl diselenides,[1002] organosilicon halides,[989] and mercuric acetate.[1083] Disulphides of formula $RSSCCl_3$ and tertiary phosphites are reported to form compounds with the formula $RSSC[PO(OR)_2]_3$.[1707] Some of these reactions are shown in Chart XVI.

The quasiphosphonium salts formed as intermediates in these reactions are difficult to isolate. Recently, relatively stable crystalline double salts of the type $[(RO)_3PSR]^+SbCl_6^-$ have been obtained by Hilgetag and Teichmann from the reaction of lower trialkyl phosphites with alkyl sulphenyl chlorides in the presence of $SbCl_5$.[1003]

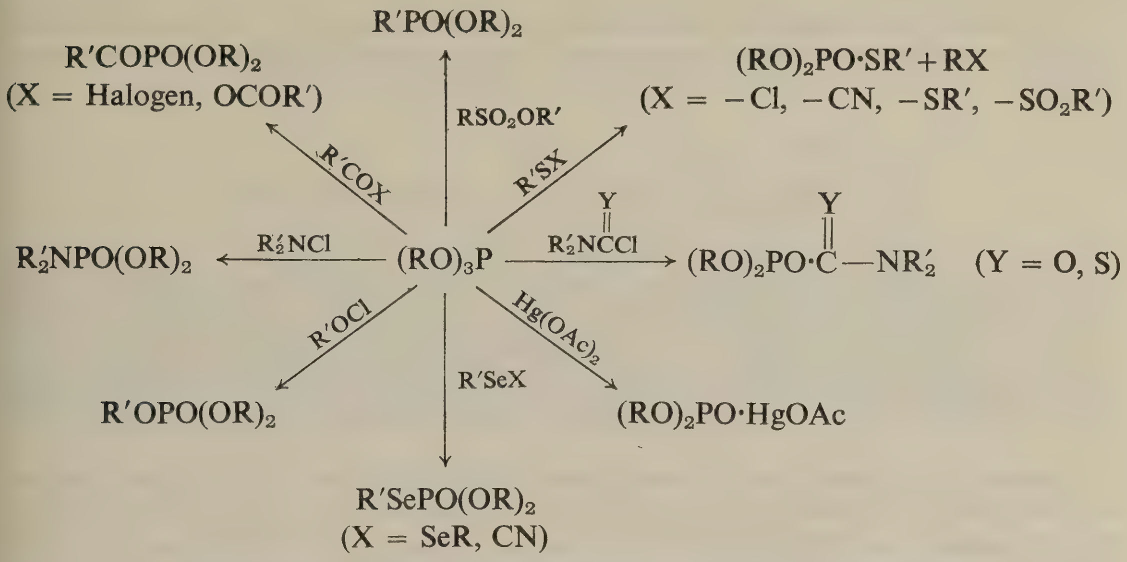
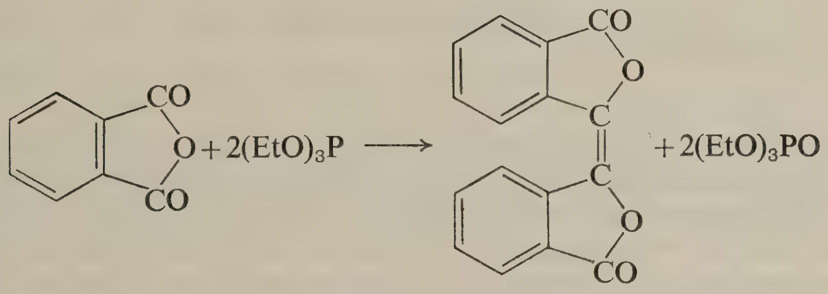
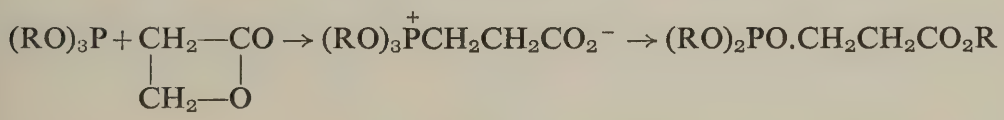


CHART XVI.—Some reactions related to the Arbuzov reaction

In contrast to the reaction of aliphatic acid anhydrides, phthalic anhydride reacts with trialkyl phosphites giving biphthalyl[885]; if the reaction is conducted in the presence of dialkyl phosphite the product is phthalide 3-phosphonate:



Lactones such as $\beta$-propiolactone and $\gamma$-valerolactone react at the alkyl rather than the acyl carbon atom giving charged intermediates which undergo transalkylation to yield $\omega$-dialkyl phosphonocarboxylic esters[755, 1061]:

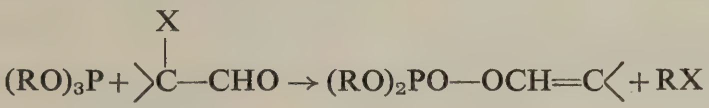


$$(RO)_3P+\begin{array}{l}CH_2\text{—}CO\\ |\qquad\quad |\\ CH_2\text{—}O\end{array}\rightarrow (RO)_3\overset{+}{P}CH_2CH_2CO_2^- \rightarrow (RO)_2PO.CH_2CH_2CO_2R$$

By contrast, the sodium dialkyl phosphonates react at both alkyl and acyl carbon atoms giving a mixture of products.[755]

THE PERKOW OR ANOMALOUS ARBUZOV REACTION

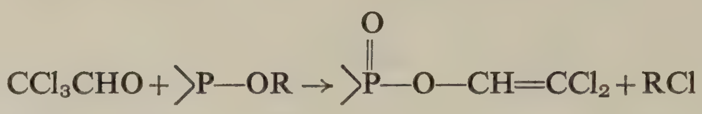
Perkow *et al.* in 1952[1010] found that $\alpha$-halogenoaldehydes did not react with trialkyl phosphites by the Arbuzov–Michaelis reaction but that a new type of rearrangement occurred yielding a dialkyl vinyl phosphate:



$$(RO)_3P+{>}\overset{X}{\overset{|}{C}}\text{—}CHO\rightarrow(RO)_2PO\text{—}OCH{=}C{<}+RX$$

The historical development leading to the recognition of the Perkow reaction, its scope and limitations, and possible reaction mechanisms have been reviewed by Lichtenthaler.[1007]

Like the Arbuzov reaction, the Perkow reaction has proved to be a general reaction for trivalent phosphorus compounds of the type R′R″POR. Reactions with chloral,



$$CCl_3CHO + \rangle P{-}OR \rightarrow \rangle \overset{O}{\overset{\|}{P}}{-}O{-}CH{=}CCl_2 + RCl$$

have been reported for the following: trialkyl and mixed trialkyl phosphites,[1013] aryl dialkyl phosphites,[1013] diaryl alkyl phosphites,[1013] *O*,*O*,*S*-trialkyl phosphorothioites,[1033] dialkyl phosphoramidites,[1030, 1191] alkyl phosphorodiamidites,[1030] dialkyl esters of phosphonous acids,[419, 1031] *O*-alkyl-*N*,*N*-dialkyl phosphonamidites,[419] alkyl esters of phosphinous acids,[419] and alkyl ethylene, tri- and tetra-methylene phosphites.[1013, 1032]

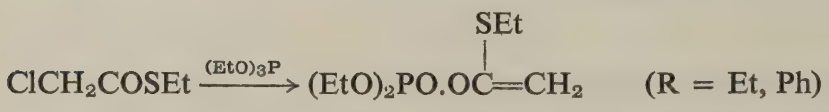
Frequently it is found that a given halogen compound reacts by both the Arbuzov and the Perkow reactions giving a mixture of products. Structural factors, the nature of the halogen and temperature have a marked influence on the relative extents of the two reactions.[1017] Whereas α-monohalogen,[946, 1013] α-dihalogen,[1013–5] and α-trihalogen[908, 1010, 1013, 1016] aldehydes react with trialkyl phosphites to give exclusively the vinyl phosphates, α-halogenoketones give mixtures of vinyl phosphate and ketoalkyl phosphonate.[1012, 1017–8] Thus chloro-, bromo- and iodo-acetones give mixtures of *O*,*O*-dialkyl-2-ketopropyl phosphonate and dialkyl 1-methylvinyl phosphate[1017]:

$$(RO)_3P + XCH_2COCH_3 - \begin{cases} \rightarrow (RO)_2PO.CH_2COCH_3 + RX & \text{(Arbuzov)} \\ \rightarrow (RO)_2PO.{-}OC(CH_3){=}CH_2 + RX & \text{(Perkow)} \end{cases}$$

Chloroacetone reacts predominantly by the Perkow reaction, bromoacetone gives a mixture of products and iodoacetone yields predominantly the phosphonate. Higher reaction temperatures favour the occurrence of the Arbuzov reaction over the Perkow reaction.[1017] Ketones in which the halogen atom is attached to a secondary carbon atom react to a significantly greater extent by the Perkow reaction than those having halogen on a primary carbon atom.[729, 1012, 1018] Ketones having more than one halogen attached to the α-carbon atom,[946, 1018] and 2-halogeno-1,3-diketones,[1022–3] react almost exclusively by the Perkow reaction.

Marked effects of structure on the course of reaction have been observed with α-halogen derivatives of fatty acids. Ethyl chloroacetate and α-halogenoacetamides[460, 960] react by the Arbuzov reaction giving phosphonate products whereas *S*-esters of α-chlorothiolacetate[1028, 1724] give largely the product formed by the Perkow reaction:

$$ClCH_2COY \xrightarrow{(EtO)_3P} (EtO)_2PO.CH_2COY \qquad (Y = NH_2, NEt_2, OEt)$$

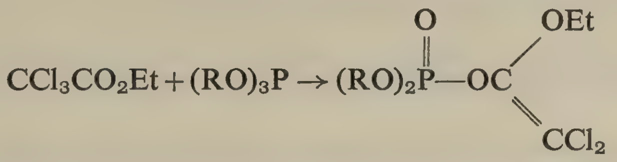


$$ClCH_2COSEt \xrightarrow{(EtO)_3P} (EtO)_2PO.O\overset{SEt}{\overset{|}{C}}{=}CH_2 \qquad (R = Et, Ph)$$

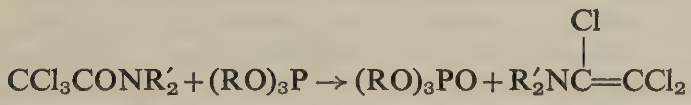
α-Halogen acetoacetates and acetoacetamides react according to the Perkow reaction[1007, 1013, 1023, 1027] as do diethyl chloro- and diethyl dichloro-malonates, ethyl cyanoacetate,[1025] and α-chloro-α-diethyl phosphonoacetone,[1027] but diethyl bromomalonate can react either by the Perkow[1020] or the Arbuzov[1024] reaction depending on the reaction conditions.

Ethyl trichloroacetate undergoes the Perkow reaction giving a dialkyl 1-alkoxy-

2,2-dichlorovinyl phosphate,[960, 1013, 1020] but with trichloroacetamides the major reaction products are trialkyl phosphate and a trichlorovinylamine[1021]:



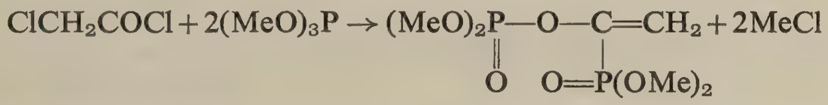
$$CCl_3CO_2Et + (RO)_3P \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}—OC(OEt)=CCl_2$$



$$CCl_3CONR'_2 + (RO)_3P \rightarrow (RO)_3PO + R'_2N\overset{\overset{Cl}{|}}{C}=CCl_2$$

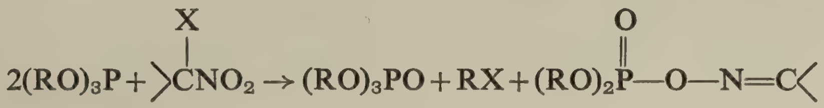
*sym*-Dichlorotetrafluoroacetone $(CF_2Cl)_2CO$ and trialkyl phosphites undergo the Perkow reaction but perfluoroketones give dialkyl phosphorofluoridate.[1725]

α-Halogenoacyl halides react with two molecules of trialkyl phosphite giving dialkyl 1-(dialkyl phosphono)vinyl phosphates,[1018, 1026] e.g., chloroacetyl chloride and trimethyl phosphite react according to the equation:



$$ClCH_2COCl + 2(MeO)_3P \rightarrow (MeO)_2\underset{\underset{O}{\|}}{P}—O—\underset{\underset{O=P(OMe)_2}{|}}{C}=CH_2 + 2MeCl$$

The reaction of α-halogenonitroparaffins such as trichloronitromethane and 1-bromo-1-nitropropane has been shown by Allen[972, 1029] to give phosphoric esters of oximes:



$$2(RO)_3P + {>}\overset{\overset{X}{|}}{C}NO_2 \rightarrow (RO)_3PO + RX + (RO)_2\overset{\overset{O}{\|}}{P}—O—N=C{<}$$

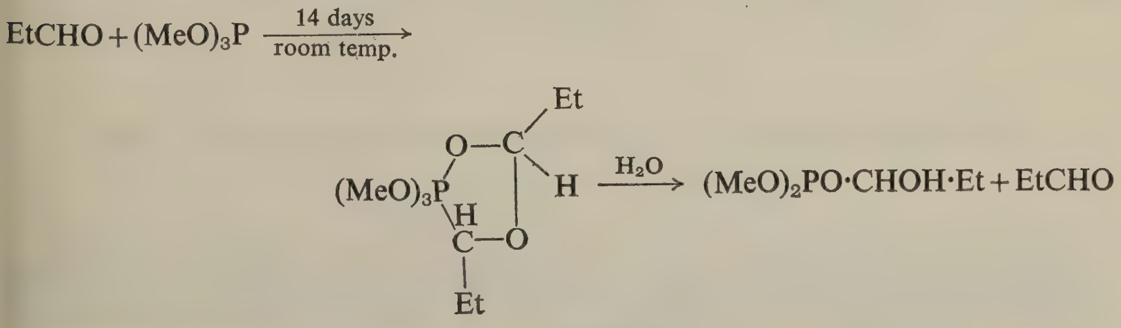
THE REACTION OF TRIALKYL PHOSPHITES WITH CARBONYL COMPOUNDS AND α-β UNSATURATED ACIDS

When aliphatic aldehydes and trialkyl phosphites are heated together in a sealed tube at 100°–170° for several hours, an Arbuzov-type reaction occurs giving a charged intermediate in which the negative charge appears on oxygen rather than on a displaced anion. This intermediate undergoes trans-alkylation to form a dialkyl 1-alkoxyalkyl phosphonate[1039]:

$$(RO)_3P + R'CHO \rightarrow [(RO)_3\overset{+}{P}CH(R')—O^-] \rightarrow (RO)_2PO.CH(OR)R'$$

Tri-*n*-propyl phosphite and benzaldehyde[1040] react to give a poor yield of di-*n*-propyl α-propoxybenzyl phosphonate; furfural yields trialkyl phosphate and difurylethylene,[1040] a reaction reminiscent of the reaction of phthalic anhydride.[885]

Ramirez and co-workers[1055] have isolated the tetraoxyalkyl phosphorane (**XVII**) in 60% yield from the reaction of trimethyl phosphite and propionaldehyde (3 moles). They consider that the initial 1 : 1 complex formed by addition of the phosphite to the carbonyl carbon of the aldehyde undergoes addition of a second mole of aldehyde giving the precursor of the oxyphosphorane. Hydrolysis of **XVII** yields dimethyl 1-hydroxypropyl phosphonate and propionaldehyde:



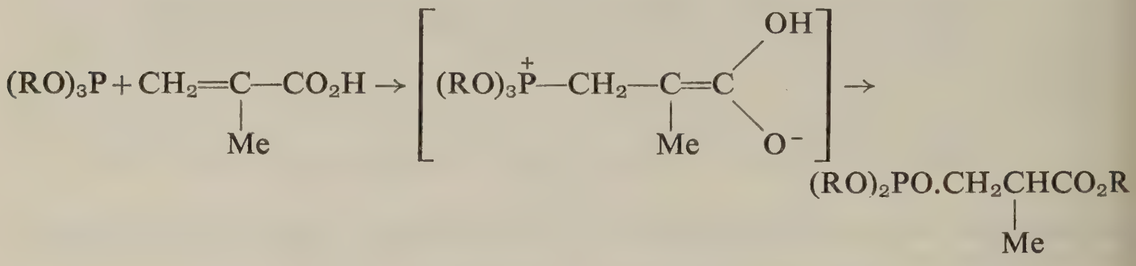
**XVII**

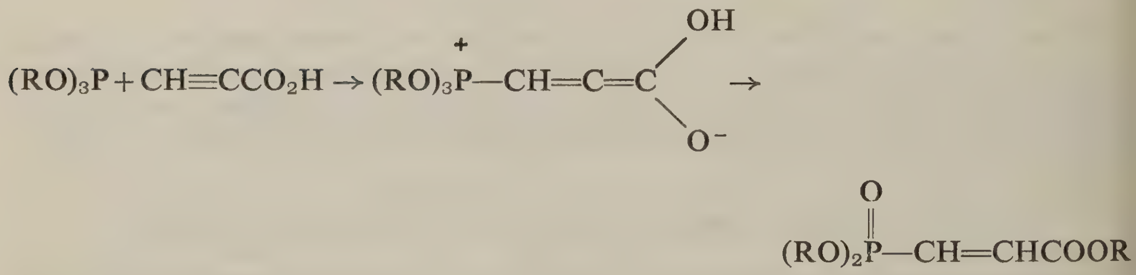
Acetone[1710] and 4-methyl-(4-dichloromethyl)-*cyclo*hexadiene-1-one[1711] are reported to be inert to triethyl phosphite. Certain aromatic ketones react with tertiary phosphites giving diarylmethylphosphonic esters,[1712] e.g.,

$$Ph_2CO + 2(RO)_3P \rightarrow Ph_2CHPO(OR)_2 + (RO)_3PO + C_3H_7 \qquad (R = \textit{iso}\text{propyl})$$

In a manner similar to the thermal reactions of aliphatic aldehydes, $\alpha$-$\beta$-unsaturated aldehydes[1041, 1044] such as acrolein and crotonaldehyde, and $\alpha$-$\beta$-unsaturated acids[1042-3] such as cinnamic acid and methacrylic acid, when heated with trialkyl phosphites, form charged intermediates in which the negative charge is transferred through the conjugated system to oxygen of the aldehyde or carboxyl group. Transalkylation results in dialkyl 3-alkoxyprop-2-enyl phosphonates and dialkyl 2-carbalkoxyethyl phosphonates, respectively. Acetylenic acids such as propiolic acid undergo the reaction at room temperature giving dialkyl 2-carbalkoxyvinyl phosphonates[1065]:

$$(RO)_3P + CH_2{=}CHCHO \rightarrow [(RO)_3\overset{+}{P}CH_2{-}CH{=}CH{-}O^-] \rightarrow (RO)_2PO.CH_2{-}CH{=}CHOR$$

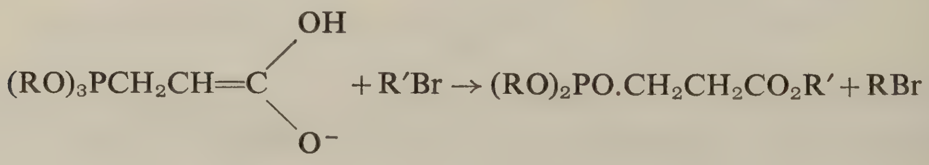




Dialkyl phosphonites react similarly with methacrylic acid giving an ester of an unsymmetrical phosphinic acid.[1045, 1062]

Kukhtin and Kamaĭ showed the rate of reaction of $(RO)_3P$ with methacrylic acid at 50° to be dependent on the nature of the solvent[1046]: polar solvents accelerate the reaction, whereas weakly polar solvents retard the reaction in comparison with the rate without solvent.

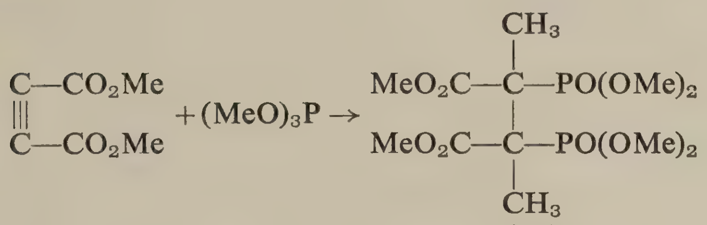
In a related reaction the combined effect of trialkyl phosphite and an alkyl halide on an $\alpha$-$\beta$-unsaturated acid yields a dialkyl 2-carbalkoxyethyl phosphonate[1046-7] by alkylation of the charged intermediate with alkyl halide:



Telomers having molecular weights ranging from several hundred to two thousand result from the reaction of triethyl phosphite and methacrylic acid in the presence of benzoyl peroxide at room temperature.[1048]

The thermal reaction of trialkyl phosphites with non-activated acetylenes proceeds through the formation of a dipolar intermediate (I) which collapses by an internal *cis* $\beta$-elimination (R = ethyl, butyl) to form olefin and vinyl phosphonate (II). Normally **II** undergoes attack by a second molecule of phosphite to form an alkylene-1,2-bis phosphonate.[2410] Dimethyl acetylenedicarboxylate and trimethyl phosphite form 2,3-bis-carbomethoxy-2,3-(dimethylphosphono)butane (III)[2409]:

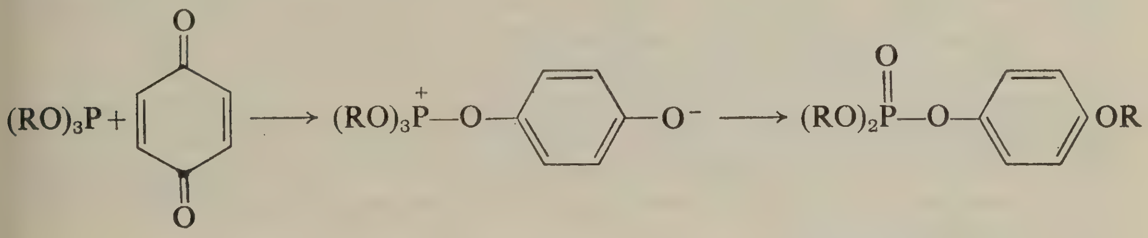
$$RC{\equiv}CH + P(OR)_3 \rightarrow \underset{\text{(I)}}{R\overset{-}{C}{=}CH\overset{+}{P}(OR)_3} \rightarrow \underset{\text{(II)}}{RCH{=}CHPO(OR)_2} + \text{olefin}$$



$$\begin{array}{l} C{-}CO_2Me \\ \| \! | \\ C{-}CO_2Me \end{array} + (MeO)_3P \rightarrow \begin{array}{c} CH_3 \\ | \\ MeO_2C{-}C{-}PO(OMe)_2 \\ | \\ MeO_2C{-}C{-}PO(OMe)_2 \\ | \\ CH_3 \end{array}$$

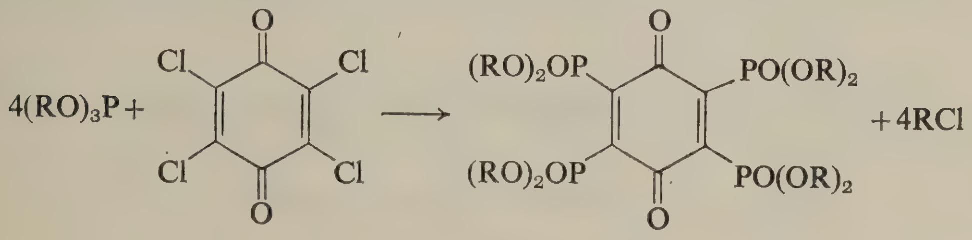
(III)

Tri(primary-alkyl) phosphites and *p*-quinones (Q) such as *p*-benzoquinone[1053] and chloranil[1054] react to give charged intermediates which undergo transalkylation yielding a dialkyl *p*-alkoxyaryl phosphate. If the reaction is conducted in the presence of water the intermediate (except that from duroquinone) is hydrolyzed to trialkyl phosphate and the quinol ($QH_2$)[1053]:



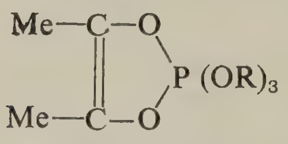
$$(RO)_3P + Q + H_2O \longrightarrow (RO)_3PO + QH_2$$

Tri(*sec*-alkyl) phosphites and chloranil react forming carbon-phosphorus rather than oxygen-phosphorus bonds, the product being a quinone 2,3,5,6-tetraphosphonate[1060]:

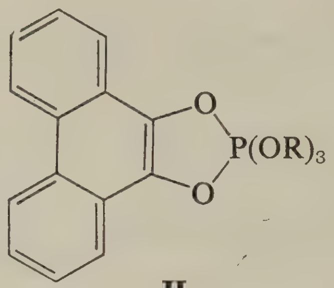


## PENTAOXOPHOSPHORANES

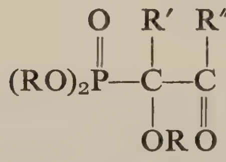
Trialkyl phosphites react at substantially room temperatures with *o*-quinones such as *o*-benzoquinone,[1066] 1,2-naphthaquinone,[1066] and phenanthraquinone,[1049, 1052] with $\alpha$-diketones such as diacetyl,[1041, 1056] benzil,[1049] and 2,3-pentanedione,[1049] and with α-ketoaldehydes to give colourless 1 : 1 adducts. Triaryl phosphites yield similar adducts if the reaction is conducted at about 100°.[1049, 1052, 1067–8] From a careful analysis of the results of Raman, infra-red, $^{31}P$ and $^{1}H$ nuclear magnetic resonance spectroscopy, and dipole moment measurements, Ramirez and Desai[1049, 1052, 1715] confirmed that the adducts are derivatives of pentaoxophosphorane. The diacetyl and phenanthraquinone adducts have structures **I** and **II**, respectively:



**I**



**II**

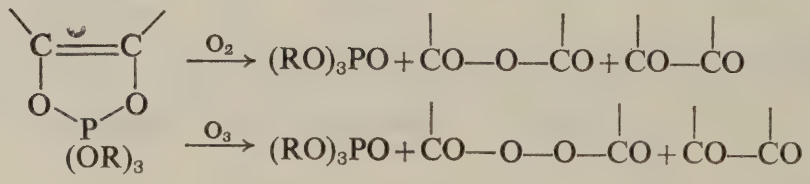


$$(RO)_2P(=O)-C(R')(OR)-C(R'')=O$$

**III**

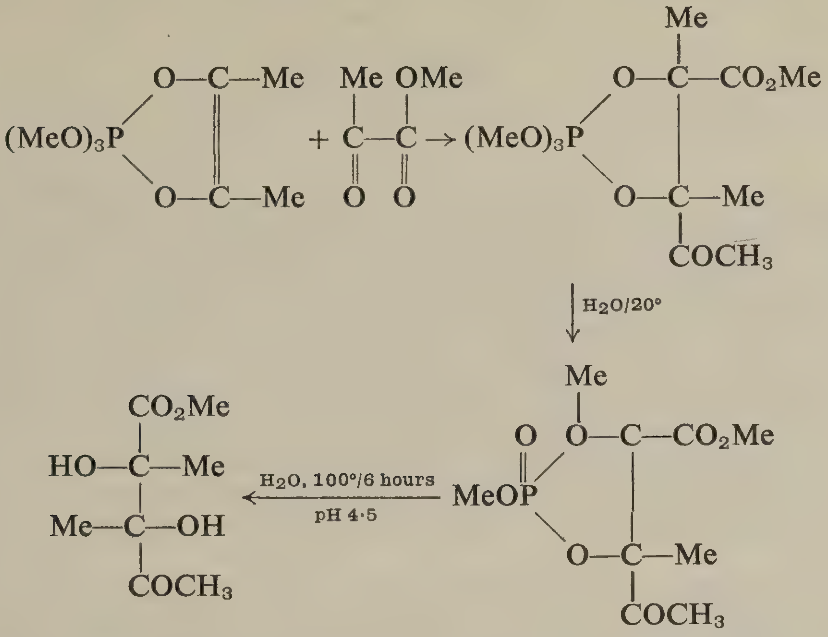
Structures of type **I** were first proposed by Kukhtin[1056] and by Birum and Dever.[1069] Although alternative structures such as **III** ($R=R'=R''=CH_3$) have been suggested by Kukhtin[1058–9] and co-workers for the reaction product of trimethyl phosphite with diacetyl, more recent work [1057, 1064, 1066] confirms the existence of compounds of type **I** and suggests that **III** ($R', R''=(CH_2)_4$, $R=Et$) is formed when *cyclo*hexanedione and triethyl phosphite interact at 120°–130°. On the other hand, near room temperature the product is an oxyphosphorane of type **I**. The formation, structure and reactions of cyclic pentaoxyphosphoranes are surveyed by Ramirez.[1716, 2411]

The pentaoxyphosphoranes do not undergo the alkyl group translocation which occurs with the adducts of trialkyl phosphites and *p*-quinones.[1052] Hydrolysis proceeds readily giving dialkyl α-ketophosphonates or dialkyl α-quinol phosphates from **I** and **II**, respectively.[1052, 1067] The adducts derived from diketones react with oxygen giving a mixture of the original diketone and an acid anhydride[1063]; ozonation of the phenanthraquinone–trimethyl phosphite adduct (**IV**, R = Me) gives a good yield of biphenoyl peroxide, trimethyl phosphate, and some phenanthraquinone[1080]:



**IV**

The 1 : 1 adduct of trimethyl phosphite and diacetyl has been shown to react further with diacetyl to give two diastereoisomeric forms of a 2 : 1 adduct having a cyclic oxophosphorane structure with a new 1,3-dioxophospholane ring system.[1051] Pyruvic acid and propionaldehyde behave similarly with the 1 : 1 adduct.[1050] On mild hydrolysis with water at 20° the ring system of the 1,3-dioxophospholane remains intact, giving a cyclic phosphate, which may be hydrolyzed under more vigorous conditions.[1715] The reactions of methyl pyruvate which lead to the formation of *DL*-threomethyl-α,β-dimethyl α,β-dihydroxylevulinate are shown below:



Non-cyclic pentaoxyphosphoranes are less well-known. Pentaphenoxyphosphorane, $(PhO)_5P$, is reported to be formed from $(PhO)_3PCl_2$ and phenol.[1718–9] (see also page 1077). Pentaethoxyphosphorane results from the reaction between triethyl phosphite and diethyl peroxide; it is unstable and decomposes slowly to diethyl ether, triethyl phosphate, and ethanol.[1717]

$$(EtO)_3P + EtO\text{—}OEt \xrightarrow[\text{temperature}]{\text{15 days at room}} (EtO)_5P$$

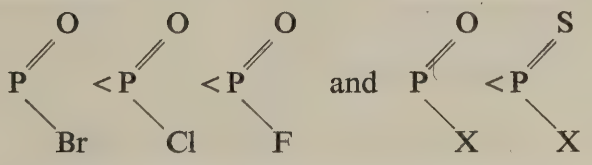
Reaction with carboxylic acid, phenol and acetylacetone, gives the ethyl ester of the acid, ethyl phenyl ether and ethyl enol ether respectively, together with triethyl phosphate.[2412]

## DERIVATIVES OF PHOSPHORIC ACID

### Esters of Phosphorohalidic Acids and Phosphorothionohalidic Acids

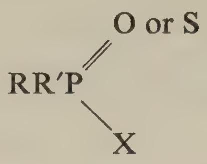
An extensive series of ester halides of phosphoric and thiophosphoric acid is known in which one or two of the halogen atoms in $POX_3$ or $PSX_3$ (X = F, Cl, Br, I) are replaced by alkoxy-, or mercaptide groups.

The lower alkyl and aryl derivatives are colourless liquids which can generally be distilled under vacuum. Vapour pressure data for a number of dialkyl phosphorofluoridates[1127, 1315] and several aryl phosphorochloridates[948, 1371] are recorded. As a class these compounds undergo fairly ready hydrolysis to the corresponding acids. The stability of the P-halogen bond in $(RO)_2POX$ or $(RO)_2PSX$ increases in the series:



Compounds of the type $(ArO)_2POF$ or $(ArO)_2PSF$ are stable in water.[1137] The hydrolysis of dialkyl phosphorochloridates to dialkyl phosphates is catalyzed by formdimethylamide.[1173]

The rates of hydrolysis of ethyl phosphorodichloridate[1035] and a number of dialkyl phosphorohalidates have been examined[438, 498, 549, 550, 1156, 1158] frequently in relation to the effect of substituents on the mechanism of hydrolysis of compounds having the general structure:



(R, R′ can be alkyl, arylalkoxyl, alkylamino, dialkylamino; X = halogen or alkoxy). The results of much of this work are collated and discussed by Hudson[1076] and are reviewed.[1171] Substitution at the phosphoryl centre normally proceeds by a bimolecular displacement mechanism with a transition state similar to an $S_N2$ displacement on carbon. Thus, Dostrovsky and Halmann demonstrated a rate sequence, $F^- > OH^- > OPh^- > EtOH > PhS^- > CH_3CO_2^-$, for the reaction of di-*iso*-propyl phosphorochloridate with anionic reagents[549] and later, in isotope studies, showed that no exchange occurs between the phosphoryl oxygen and $^{18}O$ labelled water during the hydrolysis of $(EtO)_2POCl$.[1285] In the reaction of *O*,*O*-diphenyl phosphorochloridothionate with various nucleophilic anions, the reactivities of the oxy-anions $RO^-$ and sulphur anions $RS^-$, closely follow the p*K* values of the conjugate acids.[1166-7]

Dialkyl phosphorofluoridates are extremely toxic, acting to inhibit cholinesterase. Such compounds, particularly di-*iso*propyl phosphorofluoridate (DFP), were developed as nerve gases during World War II.[1154,1172] The structural effects required to give high toxicity are discussed by Saunders.[1159] Kinetics of hydrolysis of dialkyl phosphorofluoridates,[1176] particularly DFP[438,1158,1161-4] and related toxic compounds such as sarin[1158,1160-2,1174-5,1185] and *O*-*iso*propyl methylphosphonofluoridate, have been extensively studied. Fission of the P–F bond in DFP is catalyzed by acids and bases[1164] and is accelerated by basic oxy-anions such as hydroperoxide ion,[1169] hypochlorite,[1168] and salts of oximes[1178] and of hydroxamic acids[1160,1162,1170,1230,1232] by metal ions and metal-ion complexes, particularly those of Cu(II),[1233-5] and by enzymes.[1165]

## PREPARATION

The most commonly used and simplest method of preparing phosphorohalidate esters is by reaction of an alcohol, phenol or mercaptan with an oxy- or thiono-halide of phosphorus. The ease of reaction, and the experimental technique used to obtain the product, are governed largely by three factors: (i) the nucleophilic power of the reagent towards the phosphoryl group, ROH > ArOH > RSH; (ii) the reactivity of the P–X bond in the phosphorus oxy- or thiono-halide, $POBr_3 > POCl_3 > POF_3$ and PO.X > PS.X; and (iii) the ease of dealkylation of the resulting ester by hydrogen halide formed as by-product, HBr > HCl ≫ HF(zero) and *tert*-alkyl > benzyl > *sec*-alkyl > *n*-alkyl > aryl (zero). Thus, with two active reactants such as a primary alcohol and phosphoryl chloride the chlorine atoms are rapidly replaced at essentially room temperature, whereas with less reactive pairs of compounds such as thiophosphoryl fluoride and a phenol, or phosphoryl chloride and a mercaptan[1206] it is necessary to use a tertiary organic base condensing agent. As a first approximation, the formation of primary or secondary ester halide depends on the molar proportions of reagents used as indicated by the idealized equations:

$$ROH + POCl_3 \rightarrow ROPOCl_2 + HCl \tag{1}$$

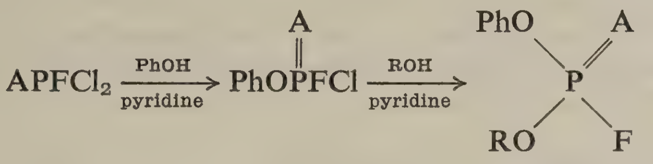
$$2ROH + POCl_3 \rightarrow (RO)_2POCl + 2HCl \tag{2}$$

Lower primary alkyl phosphorodichloridates can generally be prepared in satisfactory yield by reaction (1) carried out using an excess of phosphoryl chloride at below room temperature; the success of the preparation depends on complete removal of hydrogen chloride before distillation.[1,599,967,1133,1180] With alcohols of higher molecular weight, substantially pure alkyl phosphorodichloridates are obtained by interaction of stoichiometric amounts of alcohol and phosphoryl chloride at below 15° in vacuum.[1128,1180] The preparation of phosphorodichloridates or chloridates derived from secondary, tertiary or aryl alkyl alcohols is unsatisfactory owing to dealkylation,[1] as is the preparation of phosphorobromidates by direct reaction in the absence of a base.[902] Reaction (2) is unsuitable for the preparation of dialkyl phosphorochloridates owing to difficulties of separation from the mixture of products formed.[1181]

Dialkyl phosphorochloridates are best prepared by chlorinating the corresponding dialkyl phosphite; the bromidates may be obtained similarly but are best prepared by the action of bromine on trialkyl phosphite; for iodidates the tertiary phosphite route is essential. Phenols require temperatures higher than those for alcohols for reaction (usually at reflux) with phosphoryl chloride. Under these conditions a mixture of products forms[1139,1141] even when an excess of phosphoryl chloride is used. Phenyl phosphorodichloridate[1231] and diphenyl phosphorochloridate[1236] are readily prepared from phenol and phosphoryl chloride and can be separated easily by fractional distillation. The formation of aryl phosphorodichloridates is catalyzed by substances such as aluminium chloride,[1146,1502] salts of group I metals,[1139] calcium chloride,[1130,1134] magnesium chloride or oxide,[1] magnesium,[1126] and iron.[1140] The yield of dichloridate relative to chloridate is reduced by the presence of electron-withdrawing substituents such as chlorine in the aromatic nucleus.[1146]

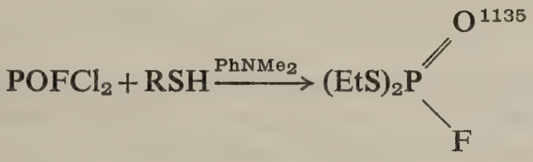
Phosphorofluoridates and chloridofluoridates have been prepared by taking advantage of the lower reactivity of the fluorine atom in phosphoryl chlorofluorides (equations 3, 4 and 5), by metathesis from the corresponding chlorides (equation 6),[1,967,1154,1177,1488] and from pyrophosphoric esters and hydrogen fluoride (equation 7).[1179]

(3)

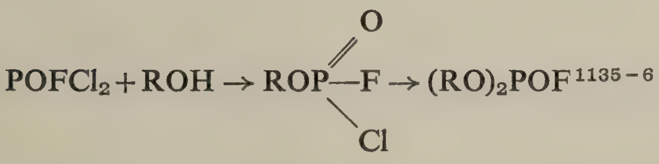


(A = O, S)[1136-8]

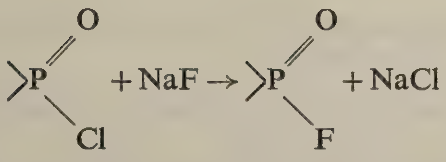
(4)



(5)

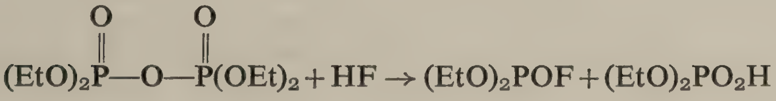


(6)



$$—POCl_2 + 2NaF \rightarrow —POF_2 + 2NaCl$$

(7)

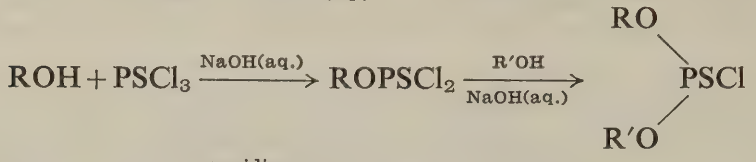


$$(EtO)_2\overset{\overset{O}{\|}}{P}—O—\overset{\overset{O}{\|}}{P}(OEt)_2 + HF \rightarrow (EtO)_2POF + (EtO)_2PO_2H$$

Thiophosphoryl chlorides react much more sluggishly with alcohols than does phosphoryl chloride, and the reaction is fairly readily restricted to the formation of alkyl phosphorodichloridothionates,[1,1152] indeed, formation of dialkyl phosphorochloridothionates and aryl phosphorodichloridothionates generally necessitates the use of a base[1230] such as aqueous alkali,[1148-50] sodium alkoxide,[1151] aluminium alkoxide[1147] or a tertiary amine[1206]:

$$ROH + PSCl_3 \rightarrow ROPSCl_2 + HCl$$

$$ArOH + PSCl_3 + NaOH_{(aq.)} \rightarrow ArOPSCl_2 + NaCl + H_2O$$



$$ROH + PSCl_3 \xrightarrow{NaOH(aq.)} ROPSCl_2 \xrightarrow[NaOH(aq.)]{R'OH} (RO)(R'O)PSCl \qquad (R, R' = \text{alkyl, aryl})$$

$$PSCl_3 + 2RSH \xrightarrow{pyridine} (RS)_2PSCl + 2HCl$$

*O*-Aryl phosphorodichloridothionates can be prepared from phenols and thiophosphoryl chloride using a catalyst such as magnesium, cuprous or phosphorous chloride, or with pyridine as a hydrogen acceptor, or from the aryl phosphorodichloridite by the reaction $ArOPCl_2 + PSCl_3 \rightarrow ArOPSCl_2 + PCl_3$.[1682] Phosphorochloridates give rather low yields of phosphorochloridothionates by treatment with phosphorus pentasulphide.[1733]

$$EtOPOCl_2 + P_2S_5 \xrightarrow[5\ hr.]{150°} EtS\text{—}PSCl_2$$

$$PhOPOCl_2 + P_2S_5 \xrightarrow[6\ hr.]{140\text{–}150°} PhOPSCl_2 + (PhO)_2PSCl + (PhO)_3PS$$

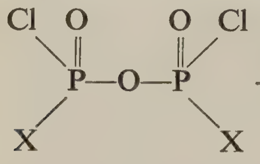
MISCELLANEOUS METHODS

Lower alkyl phosphorodichloridates have been obtained by reaction of phosphoryl chloride with trialkyl phosphates[1,600]; the method is unsatisfactory for higher alkyl compounds and for the preparation of dialkyl phosphorochloridates.[600] A high yield of diethyl phosphorochloridate is claimed from the reaction of triethyl phosphate with phosphorus pentachloride[1143]:

$$2POCl_3 + (BuO)_3PO \rightarrow 3BuOPOCl_2$$

$$PCl_5 + (EtO)_3PO \rightarrow (EtO)_2POCl + POCl_3 + EtCl$$

Pyrophosphoryl chloride and *sym*-dichlorodifluoropyrophosphoric acid react with alcohols with preferential fission of the P–O–P bond to give alkyl phosphorodichloridates[1144-5] and alkyl phosphorochloridofluoridate[1484] respectively:



$$Cl(X)P(O)\text{—}O\text{—}P(O)(X)Cl + ROH \rightarrow ROPO.XCl + HOPOXCl \qquad (X = Cl, F)$$

Alkyl or aryl phosphorohalidothionates are readily obtained by adding elemental sulphur to phosphorohalidites[1,1283]:

$$(RO)_nPX_{(3-n)} + S \rightarrow (RO)_nPSX_{3-n} \qquad (n = 1, 2;\ X = Cl, Br;\ R = \text{alkyl, aryl})$$

Alkyl phosphorochloridothioites, $RSPCl_2$ and $(RS)_2PCl$, add sulphur similarly. Frequently elemental sulphur can be replaced by thiophosphoryl chloride, which readily donates its sulphur atom to tertiary phosphites or phosphorohalidites.[1184]

Dialkyl or diaryl phosphorochloridothionates are readily obtained by chlorination of *O,O*-dialkyl(or aryl) phosphorodithioic acids or their salts, using reagents such as chlorine,[1239,1241-2] sulphur monochloride,[1238-9] sulphur dichloride,[1238] phosphorus pentachloride,[1153,1239] or sulphuryl chloride[1240]

$$2(RO)_2PS_2H + 3Cl_2 \rightarrow 2(RO)_2PSCl + S_2Cl_2 + 2HCl$$

Gerrard[1182] investigated the reaction of alcohols with phosphorus pentachloride. Primary alcohols give a mixture of alkyl phosphorodichloridate, dialkyl phosphorochloridate and alkyl chloride; secondary alcohols give higher yields of alkyl halide and olefin by-products; tertiary alcohols give almost 100% alkyl chloride. The initial chloro-esters of the type $ROPCl_4$ could not be isolated.

*S*-Alkyl phosphorodichloridothiolates are formed by the reaction of phosphorus trichloride with sulphenyl chlorides in liquid sulphur dioxide. Methyl dichlorophosphine affords *S*-alkyl methyl phosphonochloridothiolates[2417]:

$$PCl_3 + RSCl \xrightarrow[\text{at } -50°]{SO_2} RSPOCl_2$$

Reactions of dialkyl phosphorochloridates are shown in Chart XVII.

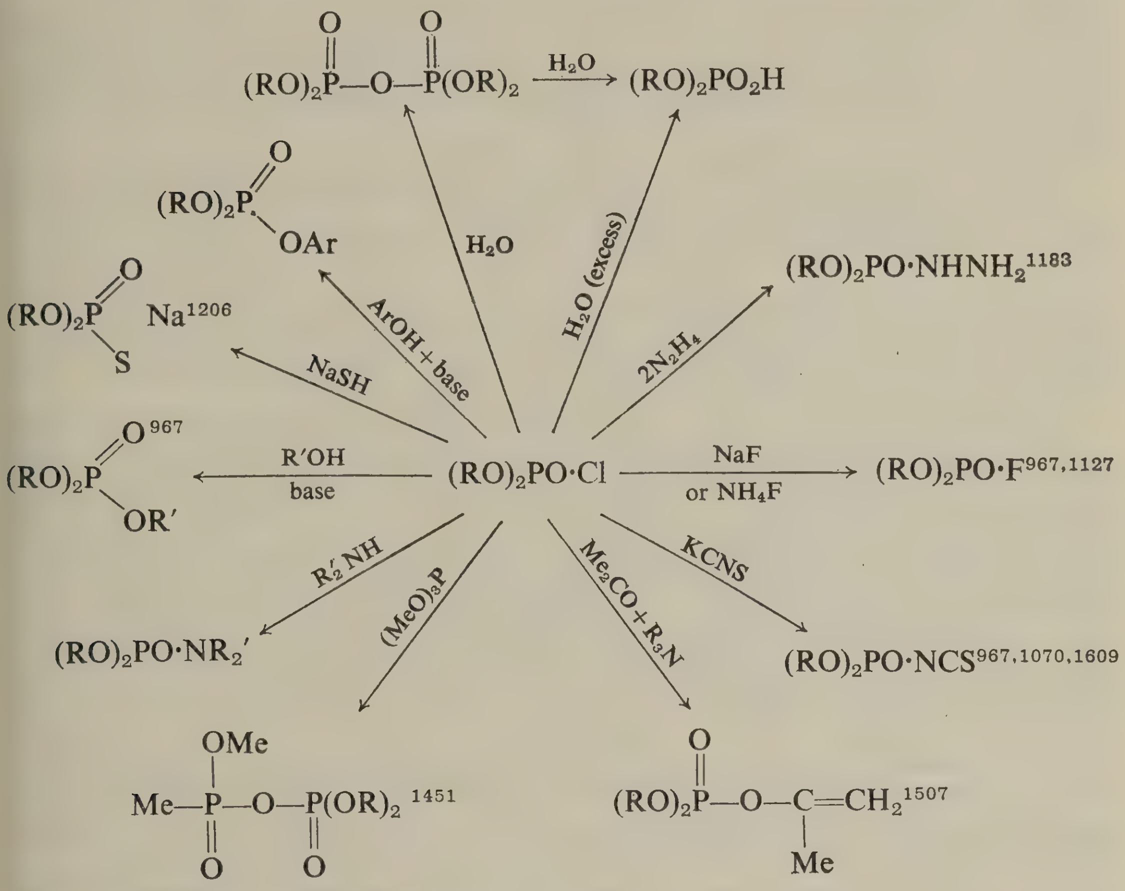


CHART XVII.—Reactions of phosphorochloridates

## ESTERS OF PHOSPHORIC ACID (AND CONDENSED PHOSPHATES AND THEIR THIO-ANALOGUES)

Esters of phosphoric acid, the condensed orthophosphates and sulphur-containing analogues form an important part of organophosphorus chemistry. Naturally occurring phosphates such as sugar phosphates, phospholipids, phosphoproteins, nucleic acids, and coenzymes, play a major role in life processes. Structural formulae of a number of the naturally occurring compounds are given by Van Wazer[3] and Hutt.[1515] Developments in the chemistry of the biologically important compounds are reviewed by Khorana,[1586] who has reported the total synthesis of coenzyme *A*.[1557] In commerce, esters of phosphoric acid have found numerous applications, most important of which are uses as plasticizers,[1516, 1530] insecticides,[1246–7, 1250, 1274, 1482, 1516, 1606] petrol and oil additives,[1216, 1218, 1243–5, 1530] extractants for metal ions,[1404, 1516–24] and as flotation agents.[1278]

There is a number of reviews concerned with phosphorylation. These may, broadly speaking, be divided into those concerned with methods[185,1193–4,1197,1200] and those concerned more with the mechanistic features of the reactions involved.[1076,1195–6]

## Mono- and Di-esters of Phosphoric Acid

### PROPERTIES

Mono- and di-esters of phosphoric acid are strong di- and mono-basic acids, respectively. The lower monoalkyl acids are stronger than phosphoric acid and the lower dialkyl acids are stronger than the monoalkyl acids; for $H_3PO_4$, $MeOPO_3H_2$, and $(MeO)_2PO_2H$, the $pK'a_1$ values are 1·97, 1·54, and 1·29 respectively.[1115] Acid strength decreases somewhat with increasing size of the alkyl substituent.[1115] Amongst the strongest phosphoric acids are the glucose 3-, 4- and 6-phosphates. Ionization constants of a number of the acids are collated by Van Wazer[3] and are correlated in terms of the Hammett $\sigma$ function of the substituent groups by Kabachnik.[1269,1274]

Association due to hydrogen-bonding is stronger in alkyl phosphoric acids than in carboxylic acids.[1403] The monobasic acids, bis(2-ethylhexyl), dibutyl, and bis(*p*-1,1,3,3-tetramethylbutylphenyl) phosphoric acids are dimeric in benzene solution, whilst the dibasic acids mono(2-ethylhexyl) and mono[*p*-(1,1,3,3-tetramethylbutyl) phenyl] phosphoric acids are polymeric. In carbon tetrachloride solution these acids show no non-associated hydroxyl spectral bands.[1403] Dimerization constants of dibutyl phosphates in organic solvents have been evaluated in connection with the use of monoacidic phosphates as extractants for metals.[1728–31]

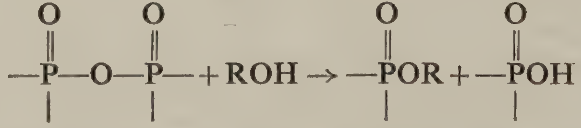
Aliphatic mono- and di-esters of phosphoric acid are syrupy liquids; the extreme water solubility of the lower alkyl acids decreases with increasing size of the alkyl substituent and from the mono- to the di-esters. Aromatic mono- and di-phosphates are frequently solids which may be crystallized from water.[1,1236] When absolutely pure (free from water, hydrogen chloride or dinitrogen tetroxide) the lower dialkyl phosphates are said to be stable at 100° and can be distilled under high vacuum.[1117–8] Acid ethyl phosphate decomposes slowly on storage; at 200° it gives triethyl phosphate and a residue of pyro- and meta-phosphoric acid esters.[1119] At 176° monobutyl phosphate undergoes extensive decomposition giving orthophosphoric acid and condensed phosphates; dibutyl phosphate is more stable but disproportionates to give approximately equal amounts (16%) of monobutyl and tributyl phosphate.[1448] Thermal decomposition of di-*n*-butyl, *sec*-butyl and *iso*butyl phosphates at 215°–302° gives butenes as the only volatile product. The volatiles from di-*n*-butyl phosphate consist of butene-1 (28%), *cis*-butene-2 (32%) and *trans*-butene-2 (40%).[1120]

The detailed crystal structure of dibenzyl phosphate has been determined by *X*-ray diffraction.[1121]

### PREPARATION

#### *Use of Anhydrides*

The earliest recorded organophosphorus compounds, crude mixtures of alkyl phosphoric acids, were prepared in 1820 by Lassaigne[1122] by heating alcohols with syrupy phosphoric acid. Anhydrides of orthophosphoric acid or its esters react with alcohols with fission of P–O–P linkages forming an ester and an acid:



$$-\underset{|}{\overset{\overset{O}{\|}}{P}}-O-\underset{|}{\overset{\overset{O}{\|}}{P}}-+ROH\rightarrow-\underset{|}{\overset{\overset{O}{\|}}{P}}OR+-\underset{|}{\overset{\overset{O}{\|}}{P}}OH$$

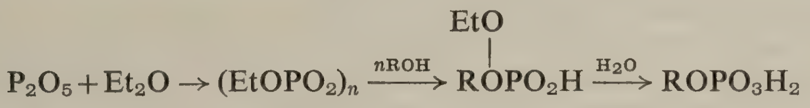
One of the simplest and commercially most important applications of this reaction is heating phosphorus pentoxide with alcohols to give approximately equimolar amounts of mono- and di-esters of phosphoric acid. The overall reaction may be written:

$$P_2O_5 + 3ROH \rightarrow (RO)_2PO_2H + ROPO_3H_2 \qquad \text{(plus traces of } H_3PO_4\text{)}$$

The reaction is generally carried out without solvent at temperatures of 30°–80°, in which range the product composition is not appreciably affected by temperature.[1330] At higher temperature some decomposition of the products occurs[1,1197] especially when secondary alcohols have been used. Colourless products are obtained by adding a small amount of hypophosphorous acid or its salts to the reactants.[1198,1329] The presence of water in the phosphorus pentoxide or alcohol leads to products having a higher monoalkyl phosphate content.[1330,1477] Products prepared in mineral oil dispersions are claimed to have low orthophosphoric acid contents.[1328]

The classical method of separating mono- and di-alkyl phosphates of lower molecular weight involved conversion of the acids into the calcium or barium salts followed by fractional crystallization from water[1,1335–6,1441]; the salts of the dialkyl phosphate are more soluble. Separation of the $C_7$–$C_{12}$ acids has been achieved by extracting the calcium or magnesium salts with a non-polar hydrocarbon to remove the salt of the dialkyl phosphate,[1331] or by extraction of the sodium salts with water to remove sodium monoalkyl phosphate.[1332] Mixtures of $C_1$–$C_9$ acids are separated by liquid–liquid extraction.[1333–4,1403–4] Bis-heptafluorobutyl phosphate may be isolated by direct distillation of the reaction mixture from phosphorus pentoxide and heptafluorobutanol.[1478–9]

'Polyphosphoric acid', a mixture of phosphorus pentoxide and 85% phosphoric acid, and the condensed phosphates obtained by heating 85% phosphoric acid, have been used extensively, particularly by Cherbuliez and co-workers, to prepare monoalkyl phosphates from substituted alcohols.[1335–8,1475] Trialkyl phosphates and phosphorus pentoxide react to give a mixture of products which is claimed, depending on the proportions of reactants used, to be predominantly alkyl metaphosphate $[(ROPO_2)_n]$, hexa-alkyl tetraphosphate $(RO)_6P_4O_4$, penta-alkyl tripolyphosphate $(RO)_5P_3O_5$ or tetra-alkyl pyrophosphate; these on hydrolysis yield mono- and/or di-alkyl phosphates.[1197,1339] The chloroform-soluble 'ethyl metaphosphate' (p. 1055) which may be prepared, following Langheld,[1398,1405] by interaction of phosphorus pentoxide and diethyl ether in chloroform, can be used to prepare phosphates from alcohols of high molecular weight.[1398,1406–7] The overall reactions may be written:



$$P_2O_5 + Et_2O \rightarrow (EtOPO_2)_n \xrightarrow{nROH} \overset{EtO}{R\overset{|}{O}PO_2H} \xrightarrow{H_2O} ROPO_3H_2$$

Monoalkyl phosphates of higher alcohols are readily prepared by reaction of the alcohol and pyrophosphoric acid[1727,2060]:

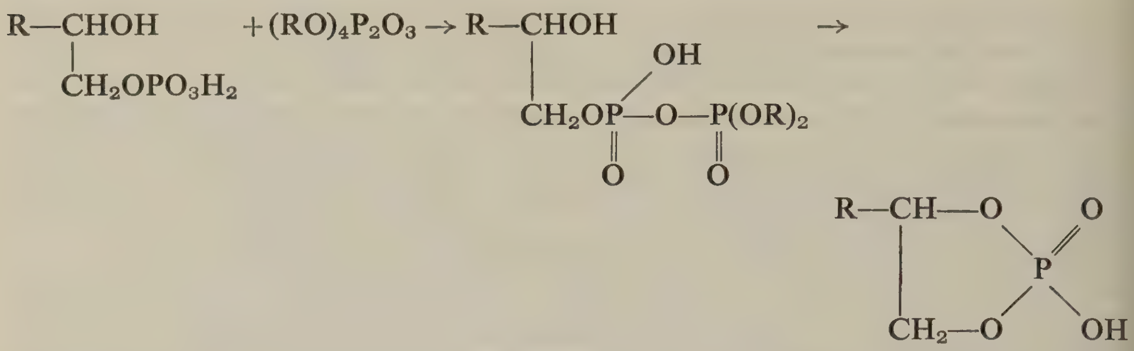
$$ROH + H_4P_2O_7 \rightarrow ROPO_3H_2 + H_3PO_4$$

Tetra-esters of pyrophosphoric acid cause phosphorylation of alcohols, usually in the presence of a base, to give mixed tertiary phosphates[1415] which, by suitable choice of substituents on the pyrophosphate, can be converted into monoalkyl phosphate by selective removal of two ester groups:

$$R'OH + (RO)_4P_2O_3 \xrightarrow{\text{base}} (RO)_2PO_2H + (RO)_2PO.OR' \rightarrow R'OPO_3H_2$$

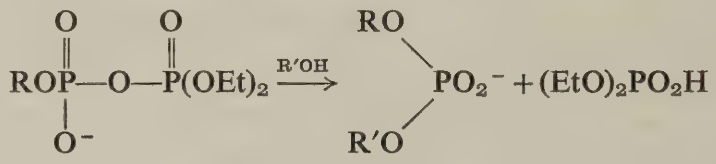
The mixed tertiary phosphates can be, and generally are, prepared by use of phosphorochloridates rather than the equivalent pyrophosphate. Alcohols can be phosphorylated with tetra-*p*-nitrophenyl pyrophosphate at room temperature in the absence of a base.[1384] One *p*-nitrophenyl group may be removed from the resulting alkyl di-(*p*-nitrophenyl) phosphate by mild alkaline hydrolysis, the second by more vigorous alkaline hydrolysis or by the action of snake venom[1410]; both *p*-nitrophenyl groups are removed by hydrogenolysis over Adams catalyst.[1384]

An interesting application of pyrophosphates is in the synthesis of cyclic phosphates from β-hydroxysubstituted phosphates. Riboflavin-4′,5′-phosphate is prepared from riboflavin-5′-phosphate with $(PhO)_4P_2O_3$ or $(PhCH_2O)_4P_2O_3$.[1411] Such reactions may be written:



Similarly a 2′- (or 3′-) nucleotide phosphate (as the trioctylamine or tridecylamine salt) with $(PhO)_4P_2O_3$ yields the nucleotide 2′,3′ cyclic phosphate.[1347] The same cyclization may be effected using trifluoroacetic anhydride[1347, 1411–2]; transient formation of a mixed anhydride of trifluoroacetic acid and the monosubstituted phosphate has been suggested.[1412–3]

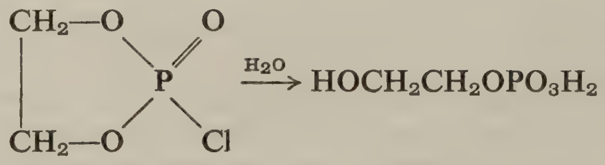
Trisubstituted pyrophosphates can cause phosphorylation of alcohols giving unsymmetrical phosphoric acid diesters[1440]:

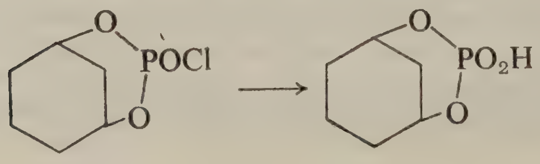


*Use of Phosphoryl Halides*

Although mono- and di-substituted phosphates can be produced by aqueous hydrolysis of the corresponding phosphorohalidates,[1, 1144, 1194, 1341, 1447–8] the method is not generally successful or practical since secondary reactions, such as hydrolysis of the ester linkages, occur so readily in the acid medium.[1194] Mono-*p*-*tert*-butyl phenyl phosphate of high purity may be obtained from the corresponding dichloridate by gradual addition of 2 moles of water at 85°–90° and removal of the hydrogen chloride formed by means of a stream of inert gas and/or reduced pressure.[1342] Frequently the phosphorohalidate, or the crude product obtained from hydroxy-compounds and phosphoryl chloride, is hydrolyzed by adding it to aqueous alkali thus giving a salt of the corresponding phosphoric acid.[620, 1117, 1448, 1525] The free acid can be obtained by adding phosphorochloridate to a suspension of the calculated amount of silver oxide in water.[1447] Dialkyl peroxyphosphates, $(RO)_2PO.OOH$, are formed by the action of pyridine and aqueous hydrogen peroxide on dialkyl phosphorochloridates.[1470]

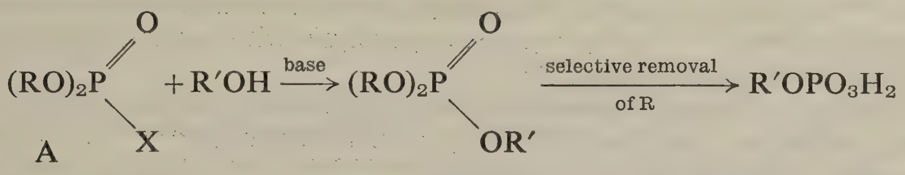
Cyclic ester halidates derived from 1,2-diols generally undergo ring fission on hydrolysis to form diol-monophosphate,[1343] but those derived from 1,3-diols give the normal product[1344]:





A number of phosphates have been obtained by adding an alcohol to phosphoryl chloride in the presence of water,[1] or to phosphoryl chloride in wet pyridine.[1345–6] Under these conditions species such as $Cl_2PO_2H$, $ClPO_3H_2$, pyrophosphoryl chloride and condensed phosphoric acid chloroanhydrides are the actual phosphorylating agents.

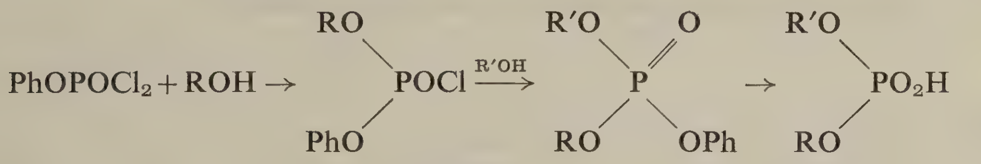
The most generally used procedure, particularly for mono- or di-phosphates of complex alcohols, is the reaction of an alcohol with a phosphorylating agent carrying protecting groups to give, usually, a tertiary phosphate from which the protecting groups are removed selectively:


A

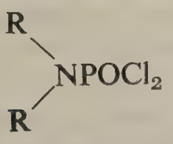
$$ROPOX_2 + 2R'OH \xrightarrow{\text{base}} ROPO(OR')_2 \rightarrow (R'O)_2PO_2H$$

B

Typical reagents, A and B respectively, are diphenyl phosphorochloridate, which has been used extensively for preparing sugar phosphates,[1193, 1236, 1348–9] and phenyl phosphorodichloridate, which is probably the most generally useful reagent for preparing symmetrical dialkyl phosphates.[1350] Unsymmetrical diesters, particularly in the phospholipid series,[1351] have been prepared from phenyl phosphorodichloridate by the following reaction sequence:



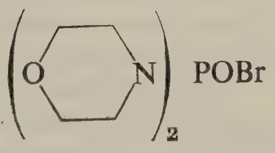
Dibenzyl phosphorochloridate has been used extensively by Todd and co-workers, particularly in the nucleotide field.[672, 1193, 1352] The reagent readily phosphorylates most primary hydroxyl groups in pyridine or, better, in 2,6-lutidine solutions[620, 1354] but is less satisfactory with secondary hydroxyl groups.[1355] It reacts with salts of phenols but not readily with the phenols themselves.[1352] Other reagents in this class, which have found specific rather than wide application are *p*-nitrophenyl phosphorodichloridate,[1356] di-*p*-bromobenzyl phosphorochloridate,[1358] di-*p*-nitrobenzyl phosphorochloridate,[1357] di-*p*-iodobenzyl phosphorochloridate,[1357] bis-(2-chloroethyl) phosphorochloridate,[1359] and bis-(2-cyanoethyl) phosphorochloridate.[1360] Similar reagents are the phosphoramidic halides,[1361–3] **I** and **II**. Amongst these compounds phosphorobromidic dimorpholide, **III**, is the most successfully used reagent.[1364]



**I**

$(R_2N)_2POCl$

**II**



**III**

### *Methods of removing the Protecting Groups*

In the preparation of complex phosphates the choice of the phosphorylating agent, and hence the mode of removing the protecting groups from the intermediate triester, is determined to a large extent by the stability of the organic residue in the final phosphate. For example, in the synthesis of nucleotides factors such as alkali lability of the 6-amino groups in cytosine, the acid lability of purine glycosidic bonds, and the catalytic reduction of pyrimidine rings must be taken into account.

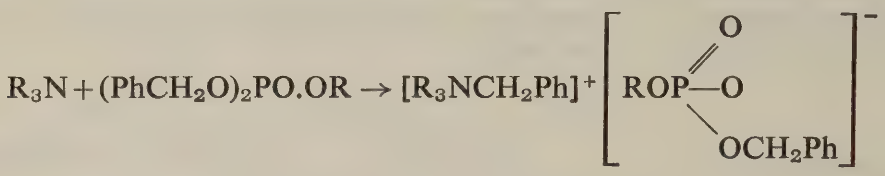
The phenyl group in monophenyl triesters may be removed by hydrogenation over platinum catalyst,[1350–1] or by alkaline hydrolysis[1365]:

$$(RO)_2PO.OPh \xrightarrow{H_2/Pt} (RO)_2PO_2H + C_6H_{12}$$

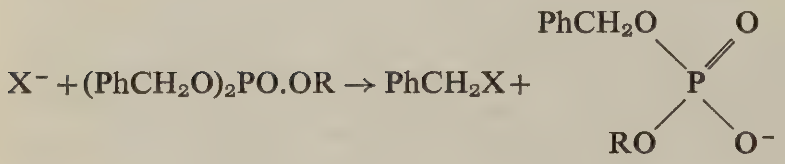
Aryl diethyl phosphates are soluble in liquid ammonia; the aryl group may be removed as aromatic hydrocarbon by reduction with lithium or sodium in ammonia solution.[1089] In diphenyl esters both phenyl groups are removed by hydrogenation over platinum,[1236, 1348–9] or by vigorous hydrolysis with barium hydroxide[1366] or with sodium carbonate solution.[1381]

The four main methods of removing protecting benzyl groups are: by hydrogenation over palladium catalysts,[1352, 1367] by acid hydrolysis,[1354, 1368] by nucleophilic displacement reactions and by phenolysis.[1366, 1369] In the last of these methods diphenyl benzyl phosphate gives diphenyl phosphate and a mixture of *o*- and *p*-benzylphenol in a ratio of 1·22:1, when heated in phenol with a catalytic amount of acid.

Particular attention has been paid by Todd and co-workers to the selective removal of one benzyl group from dibenzyl tertiary esters. Although this can be achieved by partial acid hydrolysis using dilute sulphuric acid[1354] or aqueous acetic acid,[1384] or by hydrogenolysis in the presence of a basic inhibitor,[1352, 1370] the most satisfactory and widely used methods involve nucleophilic displacements such as:

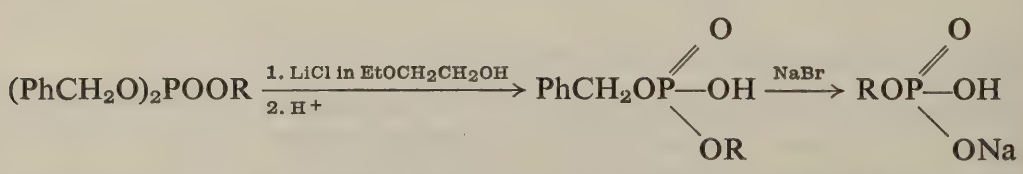


and:



(where X = Cl, OAc, NO$_3$, CNS, I)

The earliest work[620, 1372–3] using tertiary amines such as *N*-methylmorpholine and triethylamine demonstrated that neutral benzyl and substituted benzyl esters are selectively monodebenzylated giving a stable quaternary ammonium salt of a benzyl alkylphosphate. Later work with dibenzyl phosphite and tribenzyl phosphate demonstrated dealkylation by base hydrochlorides[1355] and led to the use of organic solutions of metal salts such as lithium chloride[1373–4] or potassium acetate. Thus tribenzyl phosphate is rapidly converted into lithium dibenzyl phosphate when treated with a solution of lithium chloride in ethoxyethanol at 100°. More effective reagents are sodium and barium iodides[1376, 1446, 1537, 1547] and lithium and barium thiocyanates.[1375] The use of hydrazine is reported.[1376] Two benzyl groups can be removed from ethyl dibenzyl phosphate or dibenzyl phenyl phosphate by the route[1358]:



Both 2-chloroethyl groups in a bis(2-chloroethyl)alkyl phosphate are removed by treatment with metallic sodium in dioxan.[1359] 2-Cyanoethyl groups are very smoothly removed by mild alkaline hydrolysis[1360, 1379]:

$$\mathrm{ROPO(OCH_2CH_2Cl)_2 \xrightarrow{Na} ROPO(ONa)_2 + 2C_2H_4 + 2NaCl}$$
$$\mathrm{ROPO(OCH_2CH_2CN)_2 \xrightarrow{Ba(OH)_2} ROPO_3Ba + 2CH_2{=}CHCN + 2H_2O}$$

Phosphoramidic esters can be hydrolyzed with acid.[1362, 1364, 1380]

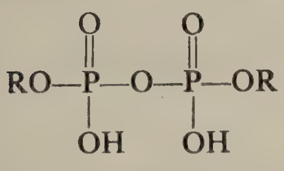
### *Use of Carbodi-imides and Related Compounds*

Carbodi-imides are of importance for the ease with which they convert acids to their anhydrides. In the organophosphorus field they have proved to be particularly valuable synthetic reagents, especially for the preparation of complex phosphates. Their use has resulted in new methods of preparation of esters of ortho-[1384–5, 1379, 1402] and pyro-[1382, 1384] phosphoric acids, cyclic phosphates,[1389–90] nucleotide coenzymes,[1391–2] and polynucleotides.[1393] The initial work by Khorana and Todd[1382] showed that under anhydrous conditions di*cyclo*hexyl (DCC) or di-*p*-tolyl carbodi-imide converts phosphate diesters to pyrophosphates; thus dibenzyl phosphate yields tetrabenzyl pyrophosphate quantitatively, while monophenyl phosphate gives *P,P′*-diphenyl pyrophosphate:

$$\mathrm{(RO)_2PO_2H + C_6H_{11}N{=}C{=}NC_6H_{11} \rightarrow (RO)_4P_2O_3 + (C_6H_{11}NH)_2CO}$$

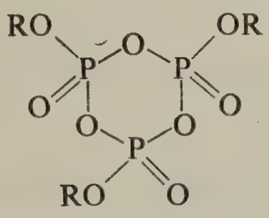
In the phosphoric acid ester field, esterification of phosphoric acid to dimethyl phosphate by reaction with an excess of methanol and DCC has been demonstrated.[1383] However, the major role of di-imides has been in the preparation of unsymmetrical diesters by condensing phosphoric acid monoesters with alcohols[1379, 1383, 1386, 1394, 1402, 1556] and of cyclic phosphates from phosphoric acid monoesters having suitably placed hydroxyl groups.[1390]

The work of Weimann and Khorana[1386] shows that monoalkyl phosphates react rapidly with DCC by way of the *P,P′*-pyrophosphate **IV** to form a trialkyl trimetaphosphate **V** which reacts slowly with alcohols giving an unsymmetrical dialkyl phosphate. Thus, ethyl phosphate and DCC in dioxan give triethyl trimetaphosphate which with methanol yields ethyl methyl phosphate in 85–90% yield. The initial formation of an *iso*urea phosphate VI, postulated by Khorana and Todd,[1382] has yet to be proven. The reaction of V with alcohols is catalyzed by DCC; thus for synthetic purposes a large excess of DCC completes the esterification in a short time[1387]:

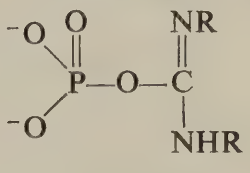


$$\mathrm{RO{-}\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}{-}O{-}\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}{-}OR}$$

**IV**

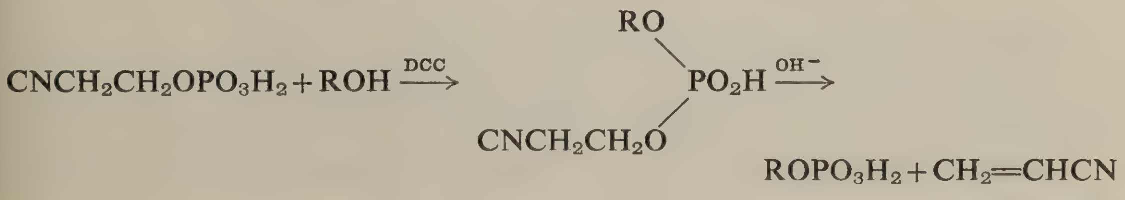


**V**

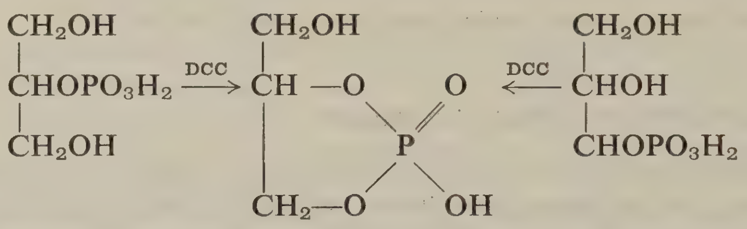


**VI**

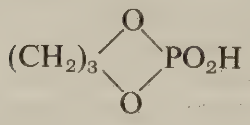
A useful procedure used to prepare $^{14}C$ labelled monomethyl phosphate and a number of nucleotide phosphates is the condensation of an alcohol with 2-cyanoethyl phosphate to form the alkyl 2-cyanoethyl phosphate which by mild hydrolysis gives monoalkyl phosphate[1379, 1555–6, 1558]:



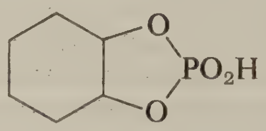
Using DCC, general methods have been developed for the preparation of 5-, 6- and 7-membered cyclic phosphates from 2-, 3- or 4-hydroxy-substituted monoalkyl phosphates, respectively.[1389-90, 1395, 1559] Glycerol α-[1395, 1397] or glycerol β-phosphate[1390] yields the same glycerol 1,2-cyclic phosphate **VII**; 3-hydroxypropyl phosphate gives the cyclic ester **VIII**[1389]; 2-hydroxy*cyclo*hexyl phosphate gives **IX**[1344]:



glycerol β-phosphate **VII** glycerol α-phosphate

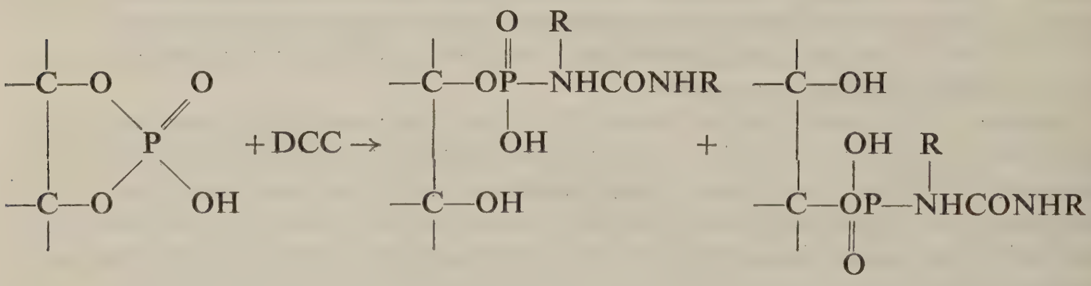


**VIII**



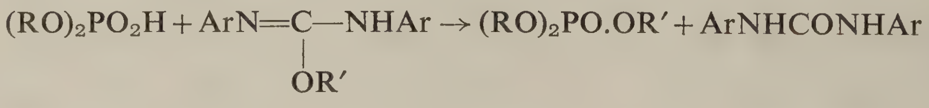
**IX**

The stereochemical requirements for cyclic phosphate formation are discussed by Khorana *et al.*[1386] 5-Membered cyclic phosphates, unlike the 6-membered compounds, undergo very ready hydrolysis and react with DCC forming *N*-phosphonyl urea phosphates[1389]:



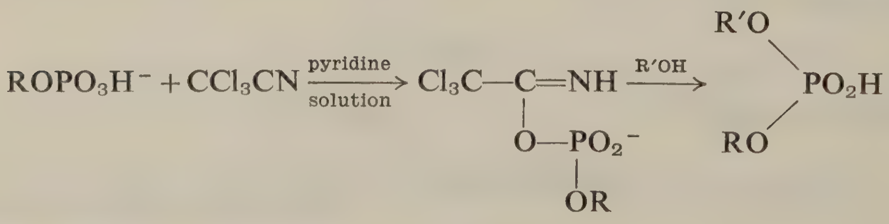
(R = $C_6H_{11}$)

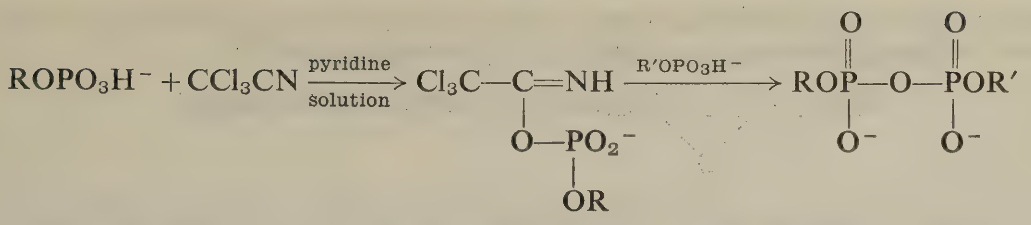
Tertiary phosphates may be prepared from secondary phosphates by reaction with an *N,N′*-diaryl-*O*-alkyl pseudourea ether (obtained from a diaryl carbodi-imide and a metal alkoxide)[1385]:



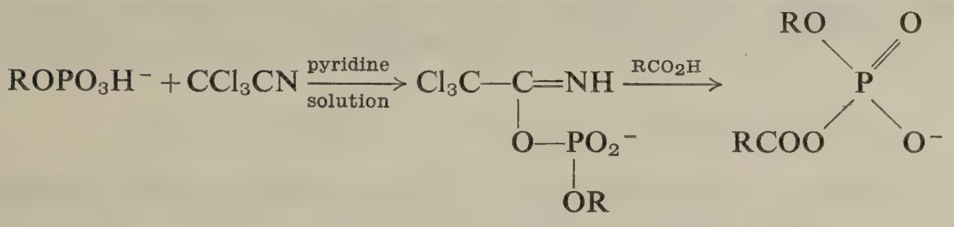
$$(RO)_2PO_2H + ArN{=}\underset{\displaystyle OR'}{\underset{|}{C}}{-}NHAr \rightarrow (RO)_2PO.OR' + ArNHCONHAr$$

The secondary acidic group in phosphoric acids is sufficiently nucleophilic to add to the nitrilo-group in trichloroacetonitrile (trichloromethyl cyanide) to form an intermediate imidoyl phosphate (cf.[1123]) formally similar to the postulated adducts formed with DCC (IX above). The intermediates react with alcohols giving unsymmetrical phosphoric diesters, with salts of monoalkyl phosphate giving *P,P′*-dialkyl pyrophosphates and with carboxylic acids giving acyl phosphates[1438-9, 1642]:

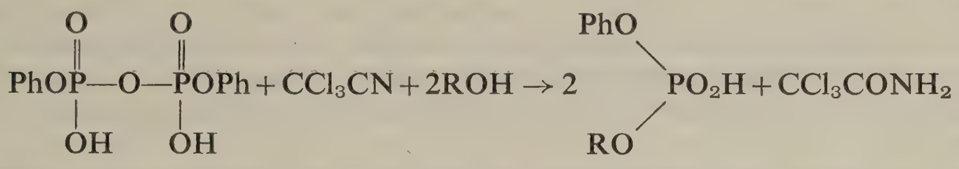




$$ROPO_3H^- + CCl_3CN \xrightarrow[\text{solution}]{\text{pyridine}} \underset{\substack{|\\ O-PO_2^-\\ |\\ OR}}{Cl_3C-C{=}NH} \xrightarrow{R'OPO_3H^-} RO\underset{O^-}{\overset{O}{P}}-O-\underset{O^-}{\overset{O}{P}}OR'$$



Phosphoric acid, benzyl alcohol, triethylamine, and trichloroacetonitrile react together similarly to give the triethylammonium salt of monobenzyl phosphate ($Et_3\overset{+}{N}H$ salt).[1439] *P,P′* diphenyl pyrophosphoric acid and alcohols react with trichloromethyl cyanide, giving alkyl phenyl phosphates[1643]:



*Miscellaneous Methods*

The reaction of alkyl halides with metal phosphates is one of the classical methods of obtaining phosphoric esters. In its original form reaction of silver phosphate with excess of alkyl halide affords a tertiary phosphate:

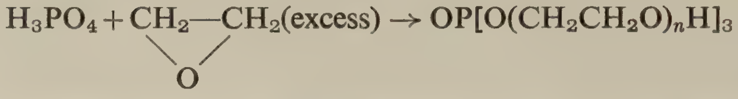
$$Ag_3PO_4 + 3RX \rightarrow 3AgX + (RO)_3PO$$

The reaction has found particular application in the preparation of sugar phosphates[1193]; thus glucose-1-phosphate has been obtained by reaction of acetobromoglucose with trisilver phosphate[1416] or with silver monophosphate[1417] (a mixture of $Ag_3PO_4$ and $H_3PO_4$). A more elegant approach has been the use of silver dibenzyl phosphate or silver diphenyl phosphate followed by removal of the protecting groups from the intermediate tertiary ester[1367, 1372, 1419, 1423] to yield the monoalkyl phosphate. Applications are for the preparation of sugar phosphates,[1418, 1427–8] phosphatidic acids,[1420–2] and uridine-5′-phosphate.[1429] Homogeneous reactions in hydrocarbon solvents may be advantageously employed if the silver salt of the diaryl phosphate is replaced by a trialkyl ammonium[1424–6, 1556, 1567] or quaternary ammonium salt.[1495]

Unlike trisilver phosphate, trisodium phosphate (or disodium phosphate and sodium hydroxide[1459]) reacts with alkyl halides[1431, 1434] or with alkyl sulphates[1432] to form mainly monoalkyl phosphates together with some dialkyl phosphates; disodium monoalkyl phosphates react similarly with alkyl halides affording sodium dialkyl phosphates[1433]:

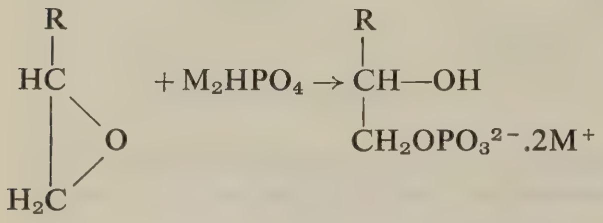
$$Na_3PO_4 + RX(\text{excess}) \rightarrow ROPO_3Na_2 + (RO)_2PO_2Na$$

Phosphates having an acidic hydrogen atom react with epoxides to give β-hydroxyalkyl phosphates. Phosphorous acid, phosphoric acid[1442, 1444] and mono- and di-alkyl phosphates[1445] react with excess of epoxides giving tertiary phosphates derived from polyalkylene glycol. These are formed by acid-catalyzed addition of alkylene oxide to the hydroxy-groups of the initially formed 2-hydroxyalkyl phosphates. Alkylene imines react similarly with phosphoric acid[1442]:



$$H_3PO_4 + CH_2{-}CH_2(\text{excess}) \rightarrow OP[O(CH_2CH_2O)_nH]_3$$

Good yields of disodium mono-$\beta$-hydroxyalkyl phosphates are obtained by reaction of disodium phosphate with epoxides such as glycidal,[1435] ethylene oxide,[1352] propylene oxide[1352] and glycidaldehyde diethyl acetal (with dipotassium phosphate) [1437]:



(R = H, Me, $CH_2OH$, $CH(OEt)_2$)

Epichlorohydrin gives glycerol-1,3-phosphate.[1193] Acid salts of monoalkyl phosphates react in a manner similar to disodium orthophosphate; thus *cyclo*hexyl ammonium 2-hydroxy*cyclo*hexyl hydrogen phosphate reacts with glycidal in boiling aqueous solution to form *cyclo*hexyl ammonium 2-hydroxy*cyclo*hexyl glyceryl phosphate.[1397] Dialkyl phosphates yield tertiary esters[1372, 1575]: thus dibenzyl phosphate and *cyclo*hexene oxide form dibenzyl *trans*-2-hydroxy*cyclo*hexyl phosphate.[1372]

The reaction of monoammonium or monosodium phosphate with glycerol at 175°–180°, a step in the preparation of calcium glycerophosphate, was examined by Bailly, who showed the initial product to consist of a mixture of $\alpha$- and $\beta$-glycerophosphate plus some diglycerophosphate.[1435–6]

Diazoalkanes readily alkylate the acidic hydroxyl groups of phosphoric acids but the scope of the reaction is limited by the availability of the required diazoalkane. Reichstein and Schindler obtained desoxycorticosterone phosphate from 21-diazoprogesterone and phosphoric acid.[1443] Generally all the acidic hydroxy-groups are alkylated; thus primary[1413] or secondary[620] phosphates yield tertiary esters. Acid salts of monoalkyl phosphates are selectively monoalkylated[1397, 1560]:

$$(PhCH_2O)_2PO_2H + R'_2CN_2 \rightarrow (PhCH_2O)_2PO.OCHR'_2 + N_2$$
$$ROPO_3H^- + R'_2CN_2 \rightarrow ROPO(OCHR'_2)O^-$$

Equilibration between orthophosphoric acid and the esters $(RO)_3PO$ (R = alkyl or aryl) proceeds readily under the influence of heat.[1527] Equimolar quantities of the acid and $(PhO)_3PO$ give an initial product containing up to 70% equimolar quantities of $(PhO)_2PO_2H$ and $PhOPO_3H_2$; the 4-component system then undergoes further equilibration.[1527]

$^{32}P$-labelled $BuOPO_3H_2$ and $(BuO)_2PO_2H$ have been prepared by equilibration of $H_3{}^{32}PO_4$ with $(BuO)_3PO$ at 176°.[1448]

## Tertiary Phosphate Esters

As a class, tertiary phosphates possess a fairly high degree of thermal stability. Decomposition to olefins, which is catalyzed by phosphoric acid and decomposition products,[1527] occurs on pyrolysis at temperatures above about 300°C.[1180, 1527, 1660]; extensive rearrangement of the double bond in the olefin occurs.[1660]

The following physico-chemical properties of the simpler tertiary phosphates are recorded: vapour pressures,[1323, 1353, 1371, 1378, 1396] dipole moments,[196, 876, 1654–6] enthalpies of formation of triethyl and tripropyl phosphates,[1530] surface tension and parachors,[771–3] specific molecular rotativities and magnetic susceptibilities,[1659] molecular and bond refractions,[1657] polarographic half-wave potentials[1658] and $^{31}P$

nuclear magnetic resonance shifts. Corresponding values relating to phosphorothionates, phosphonates, phosphites, etc., are given in many of the papers.

Compounds having a phosphoryl group have the ability to extract many cations, including those of the lanthanides, actinides, and zirconium, from aqueous acidic solution.[1404, 1516–24, 1644–53, 1728–32] Tributyl phosphate (TBP) is well established as an extraction solvent for uranium in the chemical processing of nuclear fuels,[1644, 1649] and for thorium and many other metals. Its extraction properties have been extensively studied. The following equilibrium is established for uranium extraction from aqueous nitric acid solution[1649–50, 1652]:

$$UO_2^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} + 2TBP_{(org)} \rightleftharpoons UO_2(NO_3)_2,2TBP_{(org)}$$

The crystal structure of $UO_2(NO_3)_2,2(EtO)_3PO$ shows the uranium atom to be 8 co-ordinate with bidentate nitrate and unidentate phosphate ligands.[1648] Extraction studies indicate that many metal nitrates exist in simple molecular complexes, $M(NO_3)_n,mTBP$, in TBP solution; for example (Y, Ce, Eu, Tb, Tm, Lu, Am) $(NO_3)_3,3TBP$, (Zr, Th, Np, Pu) $(NO_3)_4,2TBP$, and (U, Np, Pu)$O_2(NO_3)_2,2TBP$.[1562] Uranyl salt–TBP complexes having the general formula $UO_2A_2,2TBP$ (where A = Cl, Br, $NO_3$, OAc, $ClO_4$) have been identified by partition coefficient and infra-red studies. [1646, 1650]

Phosphonates are strikingly superior to phosphates for the extraction of uranium and thorium.[1545] Distribution coefficient determinations for the extraction of uranyl nitrate from aqueous nitric acid solution into solvent solutions of a number of organophosphorus compounds give the following decreasing order of extraction power[1521, 1647, 1732]: $Bu_3PO > Bu_2PO.OBu > BuPO(OBu)_2 > [(BuO)_2PO.CH_2]_2 > [(BuO)_2PO]_2CH_2 > (sec\text{-}BuO)_3PO > (n\text{-}BuO)_3PO \gg$ triallyl phosphate $\gg (BuO)_2PO.OPh \ggg (PhO)_3PO$. Thermodynamic data for the extraction of uranyl nitrate by a number of phosphates and phosphonates are given by Siddall.[1522]

Distribution studies of proton acids between TBP and aqueous phases show the formation of the following complexes in the TBP phase: $HNO_3.TBP$, $HNO_3.2TBP$, $HCl.2TBP$, $HCl.3TBP$ and $HClO_4.2TBP$.[1651]

Triethyl phosphate has been suggested as a non-aqueous solvent[1662]; spectroscopic and conductimetric studies of solutions containing anhydrous ferric chloride suggest an equilibrium containing $Fe[OP(OEt)_3]_6^{3+}$ and $FeCl_4^-$ ions. Phosphoryl compounds such as $(MeO)_3PO$, $(MeS)_3PO$, and $(Me_2N)_3PO$, have been suggested as solvents for bases in organic reactions.[1663] The boron trichloride complex of triphenyl phosphate, $(PhO)_3PO,BCl_3$, is stable at 100°[1661] but the triethyl phosphate complex decomposes at room temperature giving ethyl chloride; the triphenyl phosphite–boron trichloride complex readily undergoes rearrangement giving phosphorus trichloride and triphenyl borate (cf. ref. 1661).

The hydrolysis of phosphate esters and related compounds has recently been reviewed by Cox and Ramsay.[1171] Phosphates having a $\beta$-hydroxyl substituent readily undergo rearrangement in acid solution, the classical example being glycerol $\alpha$- and $\beta$-phosphates. The sodium salts of these acids are stable when heated in sodium hydroxide solution, but the two acids are mutually transformed into each other on heating in dilute sulphuric acid solution; at pH 0·9, $\alpha$- and $\beta$- forms are present in a ratio of 87:13.[1436, 1664, 1667] Sodium methyl $\alpha$- and $\beta$-glycerophosphates undergo reversible transformation in alkaline solution.[1665] Nitrogen to oxygen phosphoryl migrations during the acid hydrolysis of *N*-di-*iso*propyl phosphoryl derivatives of ethanolamine, serine, and threonine, are reported.[1666]

The ready availability of trialkyl phosphates has led to their use as alkylating agents. Primary arylamines are readily converted in high yield to aryl dialkylamines by heating with trialkyl phosphate[1468, 1668–70]; similarly tertiary aliphatic amines may be converted into quaternary ammonium salts,[1673] alcohols to alkyl ethers, sodium acetate to alkyl acetate,[1672] sodium hydrosulphide to mercaptans and thioethers, thiourea to *S*-alkyl isothiouronium salts,[1262] and sulphides to sulphonium salts (cf. ref. 1261). Rates of quaternization of several tertiary mines with $(MeO)_3PX$ (X = O, S, Se) and $(MeO)_2POH$ are recorded.[1673]

PREPARATION OF PHOSPHORIC ACID TRIESTERS

Commercial methods of preparing trialkyl, triaryl, and mixed alkyl aryl phosphates, and some of the uses of the compounds are reviewed by Chadwick and Watt.[1194] Many routes to unsymmetrical tertiary phosphates were indicated earlier.

Triaryl phosphates are generally prepared by the direct interaction of phosphoryl chloride and the required phenol:

$$ArOH + POCl_3 \xrightarrow{\sim 100^\circ} ArOPOCl_2 + (ArO)_2POCl \xrightarrow[\sim 200^\circ]{ArOH} (ArO)_3PO$$

Catalysts, including metal halides such as aluminium, magnesium or zinc chlorides,[1509] magnesium metal,[1126] tertiary amines[1510] and ultra-violet light[1511] have been used to speed up the reaction. Other routes to triaryl phosphates are the reaction of phenols with phosphorus pentachloride, the Schotten–Baumann type reaction between phosphorus oxychloride and solutions of metal phenoxide,[1] the reaction of diaryl sulphites with phosphorus pentachloride,[1491] and the oxidation of triaryl phosphites. The direct esterification of phosphoric acid or acid phenyl phosphates with phenols, reported by Prahl,[1456] is difficult to realize in practice. Traces of triphenyl phosphate are present amongst the products from the reaction of sodium phenoxide and elemental phosphorus.[1457] Resinous polyaryl phosphates are produced by condensing phosphoryl chloride with a monohydric phenol and then with a dihydric phenol[1130, 1458]:

$$PhOH + POCl_3 \xrightarrow{CaCl_2} PhOPOCl_2 \xrightarrow[Sn]{p\text{-}C_6H_4(OH)_2} [PhOPO.OC_6H_4O]_n$$

Trialkyl phosphates were first obtained by Vögeli in 1849[1452] by heating alcohols with phosphoric acid. Although trialkyl phosphates can be, and are, prepared by solvolysis of phosphoryl chloride in alcoholic solution, the reaction requires careful control of reaction temperature and conditions so as to avoid dealkylation of the product by hydrogen chloride[1, 599–600, 1133, 1146, 1186] and pyrophosphate formation.[1527] Solvolysis of phosphoryl chloride is assisted by the addition of a catalytic amount of phosphorus trichloride.[1142] Trimethyl phosphate can be prepared by solvolysis of phosphoryl chloride with methyl alcohol by heating in a low-boiling solvent under reflux to facilitate removal of hydrogen chloride.[1526] The most commonly used methods involve reaction of phosphoryl chloride with sodium[1] or aluminium[1508] alkoxide in an excess of alcohol as solvent or with an alcohol plus tertiary amine in a hydrocarbon solvent[1460]:

$$3RONa + POCl_3 \rightarrow (RO)_3PO + 3NaCl$$

Phosphoryl bromide reacts much more rapidly with alcohols than does the chloride but, owing to rapid dealkylation of the product by hydrogen bromide, tertiary phosphates can be prepared only when the reaction is carried out with careful temperature control in the presence of a base.[902, 1462]

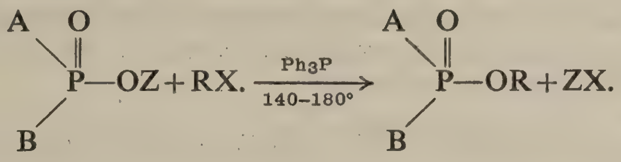
Other methods of preparing trialkyl phosphates are the pyrolysis *in vacuo* of acid salts of partial esters of phosphoric acid (for compounds up to $C_8$),[1463] oxidation of trialkyl phosphites, the reaction of trimethyl phosphate with an alkyl halide and tertiary amine catalyst,[1464] alkylation of tetra-alkyl ammonium salts of dialkyl phosphate[1495] and pyrolysis of alkyl metaphosphates or pyrophosphates,[1480] e.g.,

$$\left.\begin{array}{l}(RO)_2PO_2Na + ROPO_2Na_2\\ +(RO)_2PO_3H + ROPO_3H_2\end{array}\right\} \xrightarrow{\Delta} 2(RO)_3PO + Na_2HPO_4 + NaH_2PO_4$$

$$(MeO)_3PO + PhCH_2Cl \xrightarrow{R_3N + Na_2CO_3} (PhCH_2O)_3PO$$

$$Me_4N^+(MeO)_2PO_2^- + RX \rightarrow Me_4NX + (MeO)_2PO.OR$$

Methyl and ethyl phosphates, phosphonates and phosphinates readily undergo transesterification with alkyl halide in the presence of catalytic amounts of triphenylphosphine or tributylphosphine. The overall reaction, which is believed to proceed *via* the formation and decomposition of catalytic quantities of phosphonium salts, may be written[2285]:



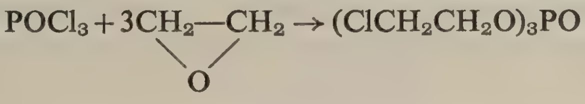
(Z = Me, Et; A = B = OR; A = alkyl, B = OR; A = B = alkyl)

The reaction of phosphorus pentoxide with ethers is complex.[1399–1401, 1498] With an excess of the ether and the olefin corresponding to R in $R_2O$, trialkyl phosphates can be made to predominate.[1493, 1496–7] Triethyl phosphate is produced commercially by heating phosphorus pentoxide with ether under an atmosphere of ethylene,[1194] the overall reaction being:

$$P_2O_5 + 3Et_2O \xrightarrow{180°} 2(EtO)_3PO$$

Ethyl orthoformate and phosphorus pentoxide react somewhat similarly; the products are triethyl phosphate, tetraethyl pyrophosphate, and ethyl formate.[1465] Tetraphosphorus decasulphide gives triethyl phosphorodithioate.[1465] Phosphorus pentoxide, or tetraphosphorus decasulphide, and olefin oxides react giving products which, depending on reaction conditions, can be water soluble 'monomers' or sparingly soluble 'polymers'.[1476]

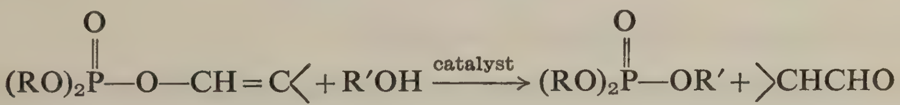
Tris-$\beta$-halogenoalkyl phosphates are readily formed from phosphorus oxychloride or bromide and olefin oxides[1500] in the presence of catalysts such as hydrogen chloride,[1492] phosphorus trichloride,[1142] aluminium chloride,[1499] zirconium or titanium chlorides[1501]:



Transesterification of phosphate esters does not, as a general rule, proceed satisfactorily. Exchange occurs readily in the presence of metal alkoxide catalyst but the catalyst is rapidly destroyed with formation of ether[1466–8]:

$$(RO)_3PO + R'OH \xrightarrow{R'O^-} (RO)_2PO.OR' + ROH$$
$$(RO)_3PO + OR'^- \rightarrow ROR' + (RO)_2PO_2^-$$

(where R, R′ = Ph, Et,[1466] and R, R′ = Et, Bu[1468]). In dialkyl vinyl phosphates transesterification of the enol linkage occurs readily in the presence of acid or base catalyst; the enol is liberated as the corresponding carbonyl compound[1007]:



$$(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}—O—CH{=}C\!\!< + R'OH \xrightarrow{\text{catalyst}} (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}—OR' + >\!CHCHO$$

Unsymmetrical alkyl phosphates may be obtained by equilibrating the appropriate trialkyl esters while hot, followed by fractionation[1469]:

$$(BuO)_3PO + (EtO)_3PO \xrightarrow{\Delta} (EtO)_2PO.OBu + (BuO)_2PO.OEt$$

$^{32}P$-labelled $(n\text{-}BuO)_3PO$ is conveniently prepared by heating $H_3{}^{32}PO_4$ with an excess of inactive $(n\text{-}BuO)_3PO$ at 200° for 1 hr.[1448]

Dialkyl aryl phosphates can be obtained by solvolysis of aryl phosphorodichloridate in an excess of an alcohol[1146]; more generally the Schotten–Baumann reaction between a dialkyl phosphorochloridate and phenol[1453] is used; alkyl diaryl phosphates are obtained similarly from alkyl phosphorodichloridate[1126]:

$$ArOPOCl_2 \xrightarrow{MeOH} (MeO)_2PO.OAr$$
$$(RO)_nPOCl_{(3-n)} + (3-n)ArONa \rightarrow (RO)_nPO(OAr)_{3-n} \qquad (n = 1 \text{ or } 2)$$

Dialkyl aryl phosphates are conveniently prepared from dialkyl phosphite, carbon tetrachloride and a phenol in the presence of a base or by the action of sodium aryloxide on tetra-alkyl pyrophosphate[1089]:

$$(EtO)_4P_2O_3 + ArOH \xrightarrow{aq.\ NaOH} (EtO)_2PO.OAr + (EtO)_2PO_2Na$$

### *Fluorocarbon Phosphates*

Phosphates in which the hydrogen atoms of the substituent groups are partially or completely replaced by fluorine atoms are described.[1454-5, 1477-9] Their preparation follows the usual pattern of phosphate syntheses:

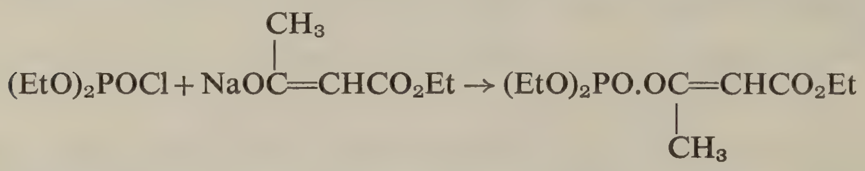
$$X(CF_2)_nCH_2OH + P_2O_5 + H_2O \rightarrow X(CF_2)_nCH_2OPO_3H_2 \qquad (X = H \text{ or } F)$$
$$(BuO)_nPOCl_{(3-n)} + (3-n)C_4F_9OH \xrightarrow{aq.\ NaOH} (BuO)_nPO(OC_4F_9)_{3-n} \qquad (n = 1, 2)$$
$$POCl_3 + 2PhOH + C_4F_9OH \xrightarrow{aq.\ NaOH} (PhO)_2PO.OC_4F_9 \text{ (main product)}$$
$$X(CF_2)_nCH_2OH + POCl_3 \xrightarrow{pyridine} [X(CF_2)_nCH_2O]_3PO \qquad (X = H, F)$$

### *Vinyl Phosphates*

The chemistry and preparation of these compounds, the enol phosphates, have been excellently reviewed by Lichtenthaler.[1007] Compounds having one vinyl ester group are normally obtained by the Perkow reaction (p. 1011) between trialky phosphite and, e.g., an $\alpha$-halogenocarbonyl compound, or by basic dehydrohalogenation and rearrangement of a dialkyl 2-halogeno-1-hydroxyalkyl phosphonate.

Other methods are the dehydrohalogenation of 2-halogenoalkyl phosphates, the reaction of enols with phosphoryl chloride[1506] or dialkyl phosphorochloridates,[1507] and the mercuric-ion catalyzed addition of dialkyl hydrogen phosphates to acetylenic compounds[1505]:

$$(RO)_2PO.OCH_2CH_2Cl \xrightarrow{NaH} (RO)_2PO.OCH{=}CH_2$$
$$POCl_3 + 3CH_3CHO + 3Et_3N \rightarrow (CH_2{=}CHO)_3PO + 3Et_3NHCl$$

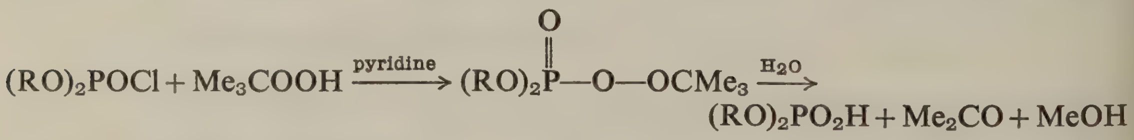


$$(EtO)_2POCl + NaO\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCO_2Et \rightarrow (EtO)_2PO.O\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCO_2Et$$

$$(RO)_2PO_2H + R'C{\equiv}CH \xrightarrow{Hg^{2+}} (RO)_2PO.OCH{=}CHR'$$

### *Phosphates containing* P–OX *bonds* (X = O, Si, Hg)

Dialkyl *tert*-butyl peroxyphosphates are readily obtained from chloridate and hydroperoxide in pyridine solution. They readily hydrolyze in water giving dialkyl phosphate, acetone and methanol[1470]:

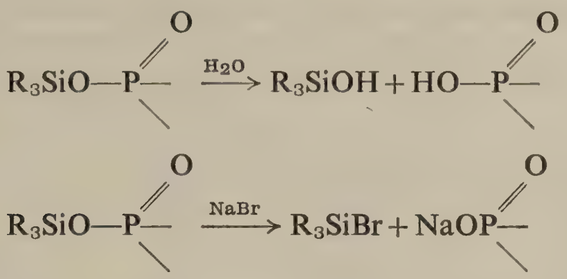


$$(RO)_2POCl + Me_3COOH \xrightarrow{pyridine} (RO)_2\overset{\displaystyle O}{\overset{\|}{P}}{-}O{-}OCMe_3 \xrightarrow{H_2O} (RO)_2PO_2H + Me_2CO + MeOH$$

Esters containing a P–O–Si group can be obtained by reaction of a hexa-alkyldisiloxane with phosphorus pentoxide, a trialkylsilyl ether with phosphoric acid, a trialkylsilyl chloride with phosphoric acid or a silicon halide with trialkyl phosphate[1471–2, 1490, 1607]:

$$P_2O_5 + 3(Me_3Si)_2O \rightarrow 3(Me_3SiO)_3PO$$

The lower alkyl compounds are distillable liquids which are readily hydrolyzed by acids or alkalis and are cleaved by heating with sodium bromide[1472]:



Tetra-alkoxysilanes yield solid hygroscopic polymers when heated with phosphorus pentoxide or phosphoryl chloride.[1473]

Ethyl mercury phosphates, $(EtHgO)_3PO$ and $(EtHgO)_2PO_2H$, can be obtained by interaction of tetraethyl lead, mercuric oxide, and phosphoric acid.[1474]

## Ester Derivatives of Phosphorothioic (Thiophosphoric) and Phosphoroselenoic Acids

### DIESTERS

Salts of diesters of phosphorothioic or phosphoroselenoic acid are readily obtained by the addition of sulphur or selenium to salts of dialkyl phosphites or by reaction with the dialkyl phosphite in the presence of ammonia or an amine. Thioic acid ester salts can also be prepared by hydrolysis of *O,O,O*-trialkyl phosphorothionate or *O,O,S*-trialkyl phosphorodithionate[1123] or from phosphorochloridate by treatment with a metal hydrosulphide.[1206] The acids themselves are obtained by treating the salt with an inorganic acid:

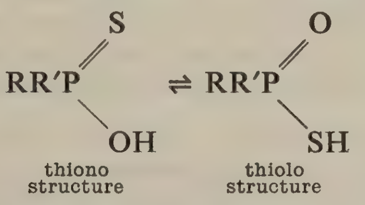
$$(RO)_2PO.H + R'_3N + S \rightarrow (RO)_2PO\bar{S}R'_3NH^+ \xrightarrow{H^+} (RO)_2PO.SH$$

$$(RO)_2PS + NaOH \rightarrow (RO)_2PO\bar{S}Na^+$$

$$(RO)_2PS.SR + NaOR' \rightarrow (RO)_2PO\bar{S}Na^+ + RSR'$$

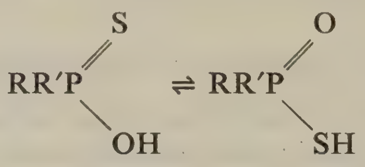
$$(RO)_2POCl + KSH \rightarrow (RO)_2PO\bar{S}K^+$$

Acids of the type RR′PO.SH (R, R′ = alkyl, aryl, alkoxy, aryloxy) exhibit a tautomeric equilibrium:



This equilibrium has been studied extensively by Kabachnik and co-workers[486, 1266–7, 1269, 1274] who have derived the equilibrium isomer concentrations from the $pK_a$ values of the monothio-acids and acids with similar substituents of the type $RR'PO_2H$ and $RR'PS_2H$, determined in 7% ethanol–water and 80% ethanol–water solvents.[1267] They find that the equilibrium is shifted to the thiono, RR′PS.OH, form and that the thiolo form appears only in noticeable amounts when the sum of the Hammett substituent constants of R and R′ ($\Sigma\sigma$) approaches zero. This effect is stronger in 7% than in 80% $EtOH–H_2O$. Results for some representative compounds are shown in Table VII.[1269]

*Table VII.—Effect of Structure on the Equilibrium*

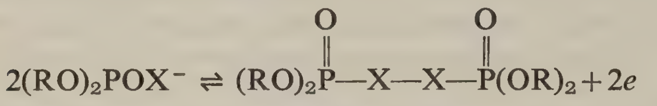


| R | R′ | $\Sigma\sigma$ | % thiolo form | |
|---|---|---|---|---|
| | | | 7% EtOH–$H_2O$ | 80% EtOH–$H_2O$ |
| EtO | EtO | −0·122 | 80 | 79 |
| MeO | MeO | −0·248 | 74 | 68 |
| PrO | PrO | −0·630 | 50 | 24 |
| Me | EtO | −1·179 | 19 | 2 |
| Ph | Ph | −1·184 | 18 | 2 |
| Et | EtO | −1·315 | 14 | 1 |
| Et | Et | −2·202 | 1 | 0·1 |
| *n*-$C_4H_9$ | *n*-$C_4H_9$ | −2·438 | 0·8 | 0 |
| *tert*-$C_4H_9$ | *tert*-$C_4H_9$ | −3·094 | 0 | 0 |

In benzene and chlorobenzene solvents p*K* measurements indicate a nearly complete shift to the thiono form.[1273]

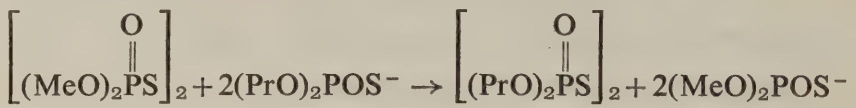
*Reactions of Dialkyl Esters and Their Salts*

Salts of dialkyl phosphorothioic or selenoic acids are oxidized by halogens to the corresponding bisdialkoxyphosphinyl disulphides (or diselenides). Foss[692] demonstrated a reversible equilibrium for oxidation with iodine and measured redox potentials in the systems:



$$2(RO)_2POX^- \rightleftharpoons (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}—X—X—\overset{\overset{\displaystyle O}{\|}}{P}(OR)_2+2e \qquad (R = \text{alkyl; } X = S, Se)$$

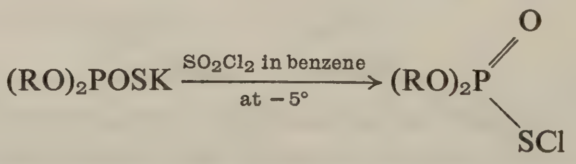
This equilibrium is progressively displaced to the right-hand side with increased electron donation of the R groups, so affording a simple route to the higher disulphides or diselenides:



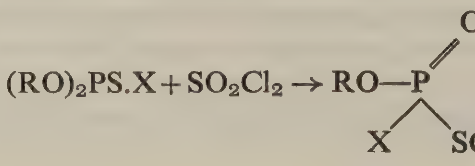
$$\left[(MeO)_2\overset{\overset{\displaystyle O}{\|}}{P}S\right]_2+2(PrO)_2POS^- \rightarrow \left[(PrO)_2\overset{\overset{\displaystyle O}{\|}}{P}S\right]_2+2(MeO)_2POS^-$$

The action of bromine on the acids or their salts yields bisdialkoxyphosphinyl disulphides (or diselenides).[692]

Chlorination of a dialkyl phosphorothioate with chlorine under controlled conditions at low temperature yields a dialkoxyoxophosphorane sulphenyl chloride.[1207] Better yields are obtained by chlorinating a salt of the acid or the corresponding bisdialkoxyphosphinyl disulphide with sulphuryl chloride[404, 1207–9]:

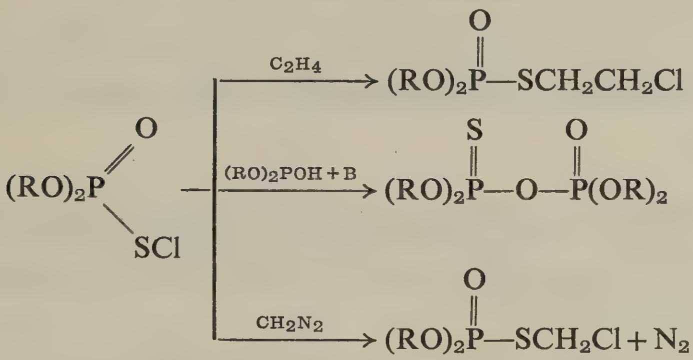


Similar compounds are obtained by chlorinating trialkyl phosphorothionates or dialkyl *N*,*N*-dialkyl phosphoramidothionates[1199]:

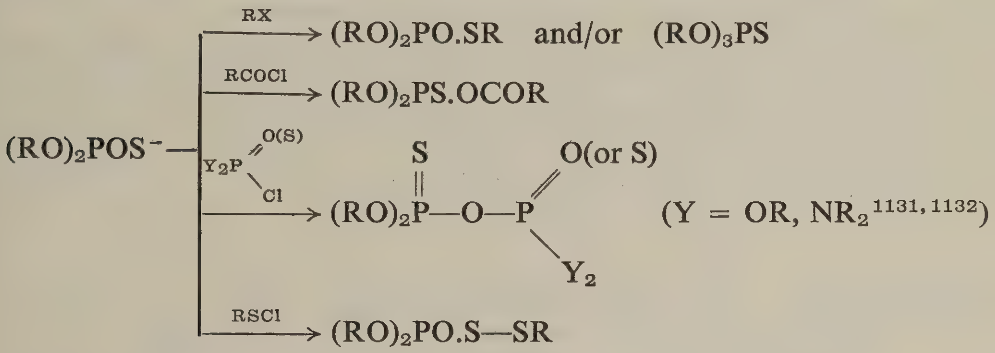


(X = OR, NEt₂)

These sulphenyl chlorides are extremely reactive. The lower alkyl compounds can be purified by distillation under good vacuum but are unstable and gradually lose active chlorine on storage, giving unidentified decomposition products.[1211] They liberate iodine from potassium iodide solution, react with alcohols, water, and amines, add spontaneously and exothermically to olefins such as ethylene or *cyclo*hexene giving *O,O*-dialkyl-*S*-2-chloroalkyl phosphorothiolates,[1207, 1209, 1211] and react with dialkyl phosphites in the presence of base giving tetra-alkyl monothiopyrophosphates,[1211] and with diazomethane to form chloromethyl thioesters[1211]:



Alkylation of dialkyl phosphorothioic acid salts can occur either on the sulphur or the oxygen atom, giving trialkyl phosphorothionates[1205] or *O,O,S*-trialkyl phosphorothiolates[1204, 1266] respectively, or a mixture of both products. Kabachnik states that alkylation invariably gives the *S*-alkyl ester.[1204] Acetylation gives the *O*-acetyl derivative.[1275] These and other reactions are shown below:



$$(EtO)_2POSH + CH_2N_2 \rightarrow \underset{\text{4 parts}}{(EtO)_2PO.SMe} + \underset{\text{1 part}}{(EtO)_2PS.OMe}^{1266}$$

$$(EtO)_2POSH + COCl_2 \rightarrow (EtO)_2POCl + COS + (EtO)_4P_2O_2S^{1225}$$

### TERTIARY ESTERS OF MONOTHIOPHOSPHORIC ACID

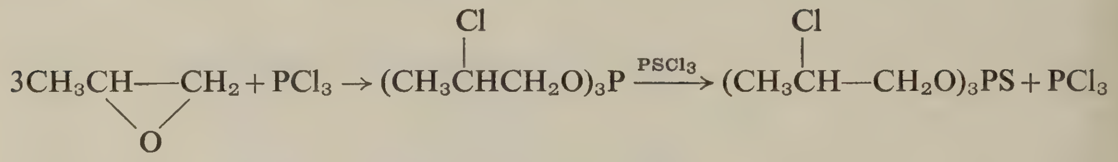
Symmetrical trialkyl phosphorothionates, $(RO)_3PS$, are conveniently obtained by reaction of thiophosphoryl chloride with alcoholic sodium alkoxide or with an alcohol in the presence of a base such as aqueous sodium hydroxide[1150, 1206]; or by adding sulphur to a trialkyl phosphite.[1289] Symmetrical compounds may be prepared by the addition of an alcohol to a mixture of sulphur and phosphorus trichloride in an inert solvent, a modification which avoids prior preparation and isolation of the phosphite.[1229]

$$3RONa + PSCl_3 \rightarrow (RO)_3PS + 3NaCl$$

Triaryl compounds can be prepared from thiophosphoryl chloride,[1148] but the reaction is sluggish.[1] A useful method which is based on the ready transfer of sulphur from thiophosphoryl chloride to triaryl phosphite involves reaction of thiophosphoryl chloride and a phenol in the presence of a catalytic amount of phosphorus trichloride[1184]:

$$\begin{gathered} PCl_3 + 3ArOH \rightarrow (ArO)_3P + 3HCl\uparrow \\ (ArO)_3P + PSCl_3 \rightarrow (ArO)_3PS + PCl_3 \end{gathered}$$

The direct reaction of thiophosphoryl chloride with alkylene oxides is unsatisfactory but proceeds readily in the presence of phosphorus trichloride. Thus propylene oxide forms tris(2-chloropropyl) phosphorothionate[1228]:

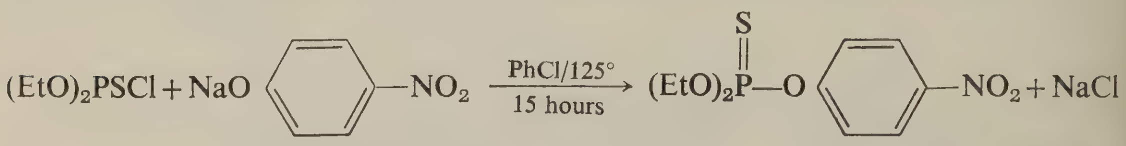


Trialkyl phosphites react exothermically with sulphur to form trialkyl phosphorothionates: $(RO)_3P + S \rightarrow (RO)_3PS$ (R = propyl, butyl, hexyl).[771] An example is the preparation of the insecticide 'Systox' by the addition of sulphur to diethyl 2-ethylthioethyl phosphite:[1289, 399]:

$$(EtO)_3P + EtSCH_2CH_2SH \xrightarrow{-EtOH} (EtO)_2POCH_2CH_2SEt \xrightarrow{S} (EtO)_2P(S)OCH_2CH_2SEt$$

Numerous compounds of the type $(RO)_2PS.OR'$ (R = alkyl; R′ = substituted alkyl, an aryl or heterocyclic residue) have been synthesized and tested as insecticides.[1151, 1230, 1247, 1264, 1282–3, 1289, 1291–8, 1449]

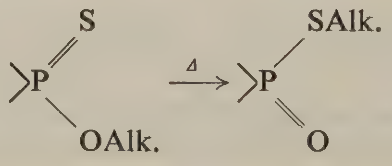
A few compounds, e.g., Parathion, *O*,*O*-diethyl-*p*-nitrophenyl phosphorothionate, and Systox, *O*,*O*-diethyl-*O*-(and *S*)-2(ethylthio)ethyl phosphorothioate, have been produced commercially for this purpose. A list of commercial phosphorothioate esters is given by Chadwick and Watt.[1194] The normal preparation involves condensation of dialkyl phosphorochloridothionate with an alcohol or phenol. Parathion was first produced in Germany by a method due to G. Schrader which involves condensing $(EtO)_2PSCl$ with dry sodium *p*-nitrophenoxide[1230]:



Catalytic amounts of tertiary amines or tertiary phosphines greatly accelerate this reaction and give high yields of Parathion.[1287] Various modifications of the basic process for manufacturing Parathion and its close analogues have been suggested. These involve the use of polar solvents such as alcohols or water to shorten reaction times,[1197] and reaction of dialkyl phosphorochloridothionate with the free phenol, sodium or potassium carbonate, and copper metal catalyst[1194, 1449] in a hydrocarbon,[1298] ketonic,[1288, 1295] chlorobenzene[1294] or aqueous solvent.[1296]

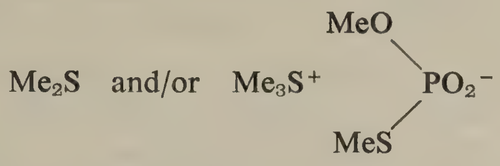
### *Isomerization*

Phosphorothionates which contain at least one *O*-alkyl substituent undergo fairly ready isomerization when heated to yield *S*-alkyl phosphorothiolate[1256, 1261, 1265]:

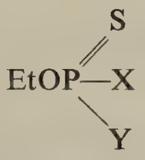


**Refs. p. 1082**

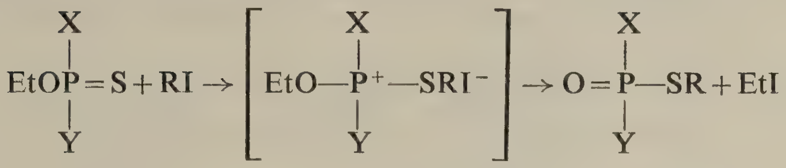
Trimethyl phosphorothionate isomerizes at 130° to *O,O,S*-trimethyl phosphorothiolate.[1256, 1261] The isomerization is catalyzed by traces of alkyl halide and by impurities in the thionate and by decomposition products



which result from alkylation of the thiolate at the sulphur atom.[1261] On heating a thionate with an alkyl halide, alkylation readily occurs on the sulphur atom yielding thiolate.[809, 1204] This has been shown to be a general reaction for compounds of the type:



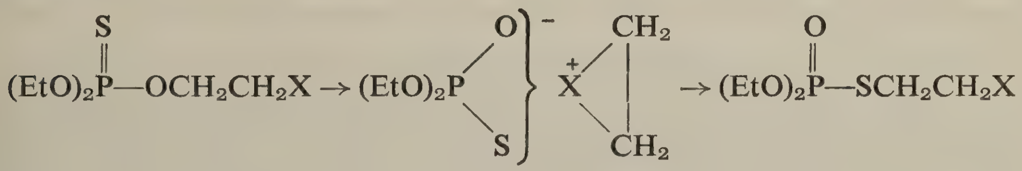
(X and Y can be R, RO, RS or $R_2N$)[1258]



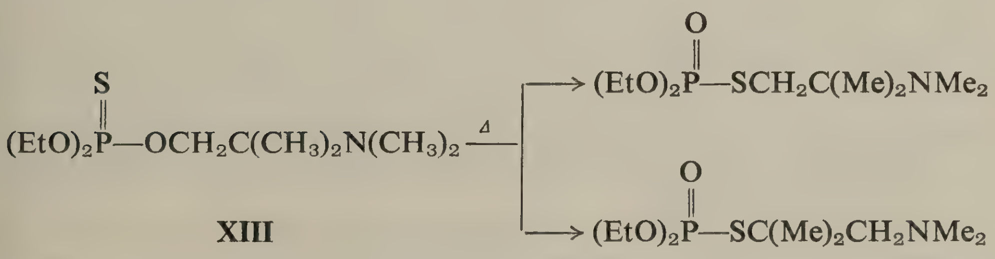
$$\mathrm{EtO}\overset{X}{\underset{Y}{P}}=S+RI \rightarrow \left[\mathrm{EtO}—\overset{X}{\underset{Y}{P^+}}—SR\,I^-\right] \rightarrow O=\overset{X}{\underset{Y}{P}}—SR+EtI$$

The alkylating properties of alkyl phosphates and thiophosphates have been reviewed.[2418]

Phosphorothionates having a $\beta$-aminoalkyl or $\beta$-thioalkyl substituent undergo facile rearrangement. Systox (**X**, where X = SEt) rearranges quantitatively at 130° to *O,O*-diethyl *S*-($\beta$-ethylmercapto)ethyl phosphorothiolate (**XII**, where X = SEt). The rearrangement is kinetically of first-order,[1263] has an activation energy of 25·4 kcal./mole[1265] and is facilitated by polar solvents.[1263, 1265] Amiton (**X**, where X = $NEt_2$) rearranges even more rapidly and can be obtained only when the temperature during its preparation is kept below 50°C.[1286] These rearrangements proceed *via* the cyclic immonium or cyclic sulphonium ion salt (**XI**, X = $NEt_2$ or SEt respectively). This has been demonstrated kinetically,[1263-4] by the lack of isomerization when formation of the cyclic ion salt **XI** is prevented as in the oxalate of Amiton or of **X** when X = SOEt,[1264] and by rearrangement of the thionate **XIII** to a mixture of isomers[1286]:



**X** **XI** **XII**


S
$(EtO)_2P—OCH_2C(CH_3)_2N(CH_3)_2$
Δ
O
$(EtO)_2P—SCH_2C(Me)_2NMe_2$
O
$(EtO)_2P—SC(Me)_2CH_2NMe_2$

**XIII**

Heavy-metal halides and silver nitrite react with trialkyl phosphorothionates at the sulphur atom, giving complexes which decompose, either at room temperature or on heating, to salts of *O*,*O*-dialkylphosphorothioic acid and alkyl halide or nitrite, respectively.[809,1299]

$$\mathrm{(MeO)_3PS + 2HgCl_2 \rightarrow (MeO)_3PS{,}2HgCl_2 \xrightarrow{102^\circ} (MeO)_2PO.S{,}HgCl{,}HgCl_2 + MeCl}$$
$$\mathrm{(RO)_3PS + AgNO_2 \rightarrow (RO)_2POS.Ag + RONO}$$

Phosphorothionates such as $\mathrm{(MeO)_2PS.SMe}$ and $\mathrm{(MeS)_2PS.OMe}$, having at least one OR group, behave similarly with mercuric chloride but trimethyl phosphorotetrathioate forms the complex $\mathrm{(MeS)_3PS{,}2HgCl_2}$, which decomposes in boiling ligroin into its constituents.[1299] Phosphoroselenoic acid esters with heavy metal halides behave similarly to the phosphorothioic acid esters.[809]

*O*,*O*,*S*-Trisubstituted phosphorothiolates are readily hydrolyzed by alkali with elimination of the –SR group; *O*,*O*,*O*-phosphorothionates are less readily hydrolyzed with loss of –OR group:

$$\mathrm{(RO)_2PO.SR \xrightarrow{NaOH} (RO)_2PO_2Na + RSH}$$
$$\mathrm{(RO)_3PS \xrightarrow{NaOH} (RO)_2POSNa + ROH}$$

The P–S–R group in thiolates is readily cleaved by chlorine or bromine; in anhydrous media dialkyl phosphorochloridate and sulphenyl chloride can be isolated,[1259] whilst in aqueous media dialkyl phosphate and sulphonyl chloride[1260] are the products:

$$\mathrm{(EtO)_2PO.SEt \xrightarrow{Cl_2} (EtO)_2POCl + EtSCl}$$
$$\mathrm{(EtO)_2PO.SEt \xrightarrow{Cl_2 + H_2O} (EtO)_2PO_2H + EtSO_2Cl}$$

### PHOSPHORODITHIOIC ACIDS

### O,O-*Dialkylphosphorodithioic and* O,O-*Diarylphosphorodithioic Acids*

Diesters of phosphorodithioic acids are very important intermediates in organophosphorus chemistry. Crude acids (80–90% pure) are produced in considerable quantity and form the starting materials for the production of a number of oil additives[1218,1243–5] and insecticides.[1246–7,1250,1279,1482] Alkali-metal and ammonium salts have been used as flotation agents,[1278] and heavy metal salts, e.g., those of barium and tin, are used as oil additives.[1216]

### *Preparation*

The crude acids are obtained by reaction of tetraphosphorus decasulphide with alcohols or phenols at temperatures generally in the range 20°–110°, depending on the reactivity of the hydroxy-compound and the stability of the dithiophosphate produced.[1129,1206,1216,1218,1223,1272,1277] The main reaction is:

$$\mathrm{P_2S_5 + 4ROH \rightarrow 2(RO)_2PS_2H + H_2S\uparrow}$$

Most primary and secondary alcohols and phenols may be converted in good yield to their corresponding dithiophosphate by suitable control of the reaction temperature and conditions. Even such reactive alcohols as *tert*-butyl alcohol and benzyl alcohol give good yields when the reaction is conducted below 45°; at higher temperatures (80°–100°) extensive decomposition occurs giving butylene and dibenzyl sulphide, respectively, as the main isolable products.[1256] Reaction of 2-methyl-2-nitro-1-propanol with tetraphosphorus decasulphide in pyridine gives the pyridine salt of *O*,*O*-bis(2-methyl-2-nitropropyl)phosphorodithionate and pyridine metaphosphorotrithioate, which by hydrolysis can be converted to phosphorothioic acid monohydrate.[1213]

Despite the importance of the dialkylphosphorodithioic acids there is little published information on the effects of the $\mathrm{ROH/P_2S_5}$ ratio, of the reaction conditions or of the history of the phosphorus sulphide on the amount and composition of the by-product neutral substances. In the reaction of ethanol with tetraphosphorus decasulphide, Bacon and LeSuer[1223] found the neutral compounds to consist of a mixture of *O,O,O*-triethyl phosphorothionate and tetra-(*O*-ethyl) trithiopyrophosphate together with small amounts of elemental sulphur and a lower sulphide of phosphorus suggested to be tetraphosphorus trisulphide. With the same reactants McIvor and co-workers[1079] report the isolation of *O,O,S*-triethyl phosphorothiolothionate and *S,S*-bis(diethyl phosphorothionyl)*O*-ethyl phosphorotrithioate $[(EtO)_2PS.S]_2PS.OEt$. Methyl and ethyl alcohols are reported to give rather poor yields of *O,O,S*-trialkyl phosphorothiolothionate.[1218]

The neutral fractions of crude methyl and ethyl phosphorodithioic acids have been examined by nuclear magnetic resonance analysis. The results, together with the approximate percentage range of composition formed in different samples, are indicated in Table VIII. Elemental sulphur was present in both the ethyl and methyl neutral fractions.[2074]

*Table VIII.—Analysis of the Neutral Fractions of Crude* O,O-*Dimethyl and Diethyl Phosphorodithionates*[2074]

| *O,O*-dimethyl | | *O,O*-diethyl | |
|---|---|---|---|
| Structure | % | Structure | % |
| $(MeO)_2PSSMe$ | 6–20 | $(EtO)_2PSSEt$ | $<2$ |
| $[(MeO)_2PS]S_2$<br>$(MeO)_2P\text{–}SH$ | 21–58 | $[EtO)_2PS]S_2$ | 19 |
| | | $(EtO)_2PSH$ | 2 |
| $[(MeO)_2PS]S$ | 27–38 | $[(EtO)_2PS]S$ | 63 |
| $(MeO)_3PS$ | 3–9 | $(EtO)_3PS$ | 6 |
| $(MeO)_2PSH$ | 7–16 | unassigned | 4 |
| unassigned | 0–11 | | |

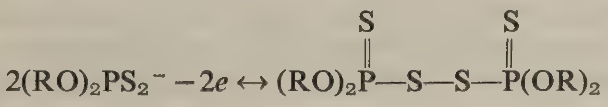
Separation of phosphorodithioic acids of lower molecular weight from the 10–20% of neutral impurities present in the crude products is readily achieved by extracting into aqueous alkali[1222] or by treating with ammonia in an inert solvent to precipitate the acid salt[1216]; these procedures are followed by careful acidification of the salt solution or the solid salt with an acid. *O,O*-Dimethyl phosphorodithioate may be ultimately purified by distillation after separation from the neutral impurities[1271] but, in general, higher alkyl compounds undergo decomposition at the temperatures required for distillation.

## *Properties and Reactions*

The phosphorodithioates are generally liquids, the lower alkyl members tending to undergo slow decomposition during storage. Salts of the acids, particularly with heavy metals, are often crystalline solids having characteristic melting points.[1254]

The lower alkyl compounds readily dissolve many metals, e.g., $(EtO)_2PS_2H$ rapidly dissolves lead, giving lead bisdiethyl phosphorodithioate and hydrogen.

Dissociation constants of a number of simple dialkyl- and diaryl-phosphorodithioic acids[1267, 1269, 1273] and 2-substituted ethyl compounds[1214] have been recorded. The atomic refraction of phosphorus and sulphur in compounds of the types $(RO)_2PS_2H$,[1212] $(RO)_2PS.SR$,[779] and $(RO)_2PS.S\text{–}SR$[779] are given by Kabachnik. Oxidation of salts of dialkylphosphorodithioic acids by iodine to bis(dialkoxythiophosphoryl) disulphides is reversible. Redox potentials for the system are given by Kakovskii *et al.*[1270]



$$2(RO)_2PS_2^- - 2e \leftrightarrow (RO)_2\overset{\overset{\displaystyle S}{\|}}{P}\text{—S—S—}\overset{\overset{\displaystyle S}{\|}}{P}(OR)_2$$

On being heated the acids decompose, giving a mixture of mercaptan, thio-ether, and olefin as volatile products. Yields of mercaptan are quite low (22·5% EtSH from $(EtO)_2PS_2H$[1256]). The reaction due to Kekulé, namely:

$$5EtOH + P_2S_5 \rightarrow 5EtSH + P_2O_5$$

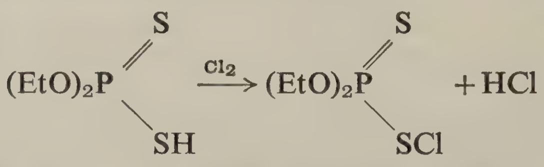
which is perpetuated in many textbooks of organic chemistry, cannot be realized under any conditions.[1273] Conversion of alcohols to mercaptans in high yield can be achieved by rearrangement of the sodium or potassium salt of the dialkyl phosphorodithioate in a polar solvent such as phenol at 180° followed by hydrolysis[1276]:

$$2ROH \rightarrow (RO)_2PS_2H \rightarrow (RO)_2PS_2K \xrightarrow[180°]{PhOH} (RS)_2PO_2K \xrightarrow[H^+]{H_2O} 2RSH$$

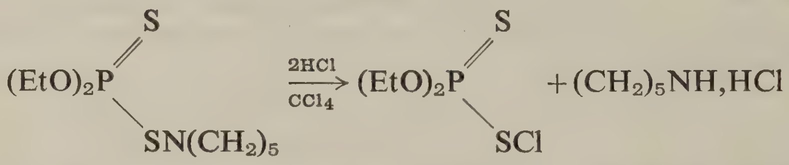
Chlorination of dialkyl- or diaryl-phosphorodithioic acids, which may be used without purification, or their metal salts or the corresponding disulphides, at 10°–40° with reagents such as chlorine,[1239, 1241–2] sulphuryl chloride,[1240] sulphur monochloride,[1238–9] sulphur dichloride[1238] or phosphorus pentachloride[1153, 1239] yields the corresponding dialkyl phosphorochloridothionates:

$$2(RO)_2PS_2H + 3Cl_2 \rightarrow (RO)_2PSCl + S_2Cl_2 + 2HCl$$
$$(RO)_2PS_2H + PCl_5 \xrightarrow{PSCl_3\ diluent} (RO)_2PSCl + HCl + PSCl_3$$

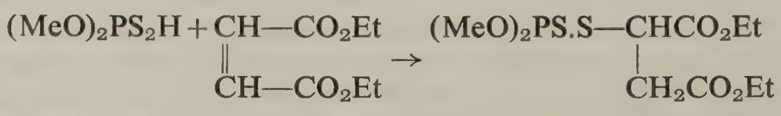
An extremely complicated set of reactions[1240] occurs and careful control of reaction temperature and of the molar proportion of chlorinating agent is necessary to obtain good yields. Controlled chlorination of $(EtO)_2PS_2H$ or $[(EtO)_2PS_2]_2$ with chlorine in carbon tetrachloride at −5° gives diethoxythionophosphorane sulphenyl chloride.[1227] Formation of sulphenyl chlorides during the chlorination:



was first proposed by Malatesta.[1242] *O,O*-Diethyl thionophosphorane sulphenyl chloride is readily obtained by the action of hydrogen chloride on *O,O*-diethyl *S*-piperidinophosphorothionothiolate[1099]:



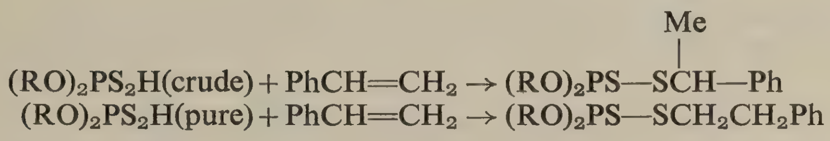
Addition of crude dialkyl phosphorodithioates to olefins has been extensively investigated because many of the adducts are commercially important as insecticides or oil additives. The insecticide Malathion is obtained by the addition of dimethyl phosphorodithioate to diethyl maleate using a small amount of a tertiary amine, such as triethylamine, as catalyst and a polymerization inhibitor such as hydroquinone[1246]:



$$(MeO)_2PS_2H + \begin{array}{l} CH{-}CO_2Et \\ \| \\ CH{-}CO_2Et \end{array} \rightarrow \begin{array}{l} (MeO)_2PS.S{-}CHCO_2Et \\ \qquad\qquad\quad | \\ \qquad\qquad CH_2CO_2Et \end{array}$$

Additions of dialkyl and diaryl phosphorodithioates to numerous unsaturated compounds are reported. Examples include ethylene[1221] and olefins of low[1218, 1223] and high[1243] molecular weight; dienes[1219, 1223, 1279]; acetylenic compounds[1513]; styrene[1223, 1249]; terpenes[1244–5]; esters of maleic and fumaric acids[1246, 1248]; chloromaleic, citraconic, itaconic esters,[1223] and related compounds[1512]; esters of methacrylic acid[1249]; acrylonitrile[1249]; vinyl alkyl sulphides,[1075] and vinyl sulphones.[1220]

The addition of crude dialkyldithiophosphoric acid to an unsymmetrical olefin gives the normal product, whereas with mercaptans addition occurs contrary to Markownikoff's rule and the addition is catalyzed by traces of peroxide in the olefin.[1222] After purification the dialkyl phosphorodithionates behave like mercaptans, giving anti-Markownikoff addition.[1219, 1222–3] It was concluded[1223] that the crude acids contain either a specific catalyst for the normal addition or a reducing agent which can destroy peroxides normally present in the olefin, thus allowing normal addition:



$$(RO)_2PS_2H(\text{crude}) + PhCH{=}CH_2 \rightarrow (RO)_2PS{-}S\overset{\overset{\displaystyle Me}{|}}{C}H{-}Ph$$

$$(RO)_2PS_2H(\text{pure}) + PhCH{=}CH_2 \rightarrow (RO)_2PS{-}SCH_2CH_2Ph$$

In the complete absence of peroxides, addition proceeds readily, giving the normal product.[1223] If addition of the pure acids to olefins is catalyzed by peroxides or ultra-violet light, the products are the same as for uncatalyzed reactions.[1219]

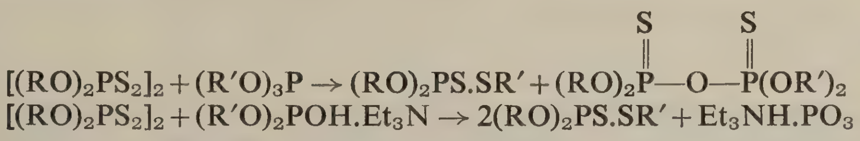
Some reactions of diesters of phosphorodithioic acids and their salts are shown on Chart XVIII.

### *Tertiary Esters of Phosphorodithioic Acids*

Most routes to the preparation of these esters have been indicated. Bis(*O*,*O*-dialkyl-thiophosphoryl) disulphides react readily with Grignard or organolithium reagents according to the equation[1514, 1674]:

$$[(RO)_2PS_2]_2 + R'M \rightarrow (RO)_2PS.SR' + (RO)_2PS_2M$$
$$(R = \text{alkyl};\ R' = \text{alkyl, vinyl, alkynyl, aryl})$$

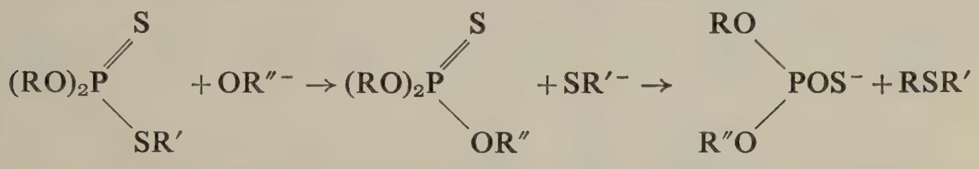
Trialkyl phosphites react giving *O*,*O*-dialkyl-*S*-alkyl phosphorodithioate and an unsymmetrical tetra-alkyl dithiopyrophosphate; salts of dialkyl phosphites also act as alkylating agents[1605]:



$$[(RO)_2PS_2]_2 + (R'O)_3P \rightarrow (RO)_2PS.SR' + (RO)_2\overset{\overset{\displaystyle S}{\|}}{P}{-}O{-}\overset{\overset{\displaystyle S}{\|}}{P}(OR')_2$$

$$[(RO)_2PS_2]_2 + (R'O)_2POH.Et_3N \rightarrow 2(RO)_2PS.SR' + Et_3NH.PO_3$$

*O*,*O*,*S*-Trialkyl phosphorothiolothionates and metal alkoxides in alcoholic solution readily form dialkyl sulphides and dialkyl phosphorothionate salts.[1223] The reaction represents an interesting example of the relative nucleophilic characters of $OR^-$ and $SR^-$ towards phosphoryl and carbon centres respectively:



The group most susceptible to nucleophilic attack is eliminated from the intermediate phosphorothionate, to appear in the dialkyl sulphide.

### ESTERS OF PHOSPHOROTRITHIOIC ($H_3PS_3O$), PHOSPHOROTETRATHIOIC ($H_3PS_4$), AND METAPHOSPHOROTRITHIOIC ACIDS ($HPS_3$)

Mercaptans react with tetraphosphorus decasulphide, giving initially alkyl metaphosphorotrithioates, which with more mercaptan yield dialkyl phosphorotetrathioates and eventually trialkyl phosphorotetrathioates[1201–3, 1255]:

$$2RSH + P_2S_5 \rightarrow RSPS_2 + H_2S$$
$$RSPS_2 + RSH \rightarrow (RS)_2PS_2H$$
$$(RS)_2PS_2H + RSH \rightarrow (RS)_3PS + H_2S$$

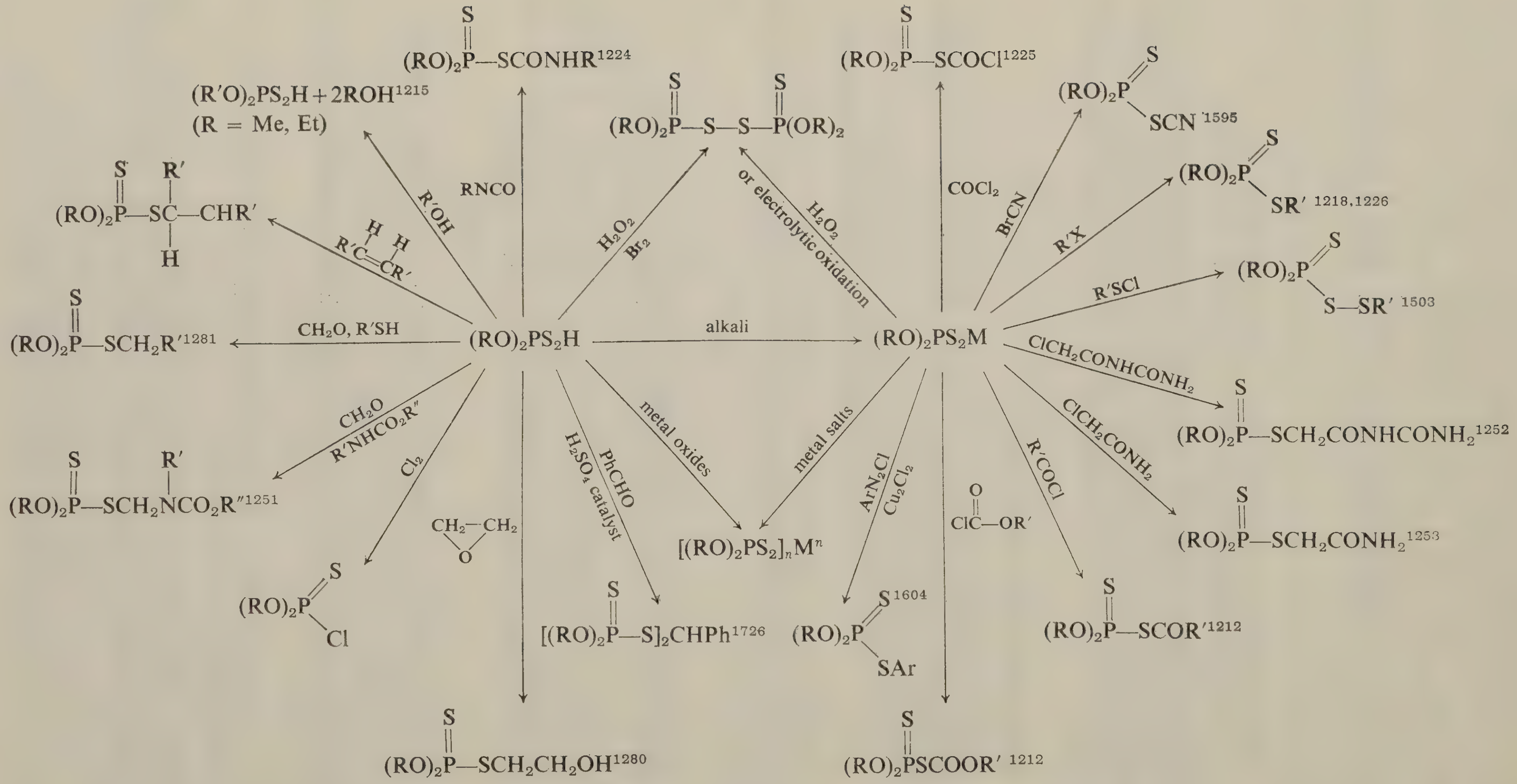
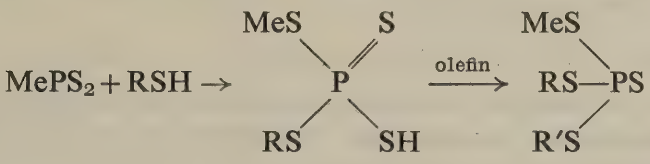


CHART XVIII.—Some reactions of diesters of phosphorodithioic acid and their salts

Methyl metaphosphorotrithioate, an insoluble crystalline solid, may be used to prepare unsymmetrical tertiary esters of phosphorotetrathioic acid[1203]:



$$\mathrm{MePS_2+RSH \rightarrow \underset{RS\qquad SH}{\overset{MeS\qquad S}{P}} \xrightarrow{olefin} \underset{R'S}{\overset{MeS}{RS{-}PS}}}$$

Dialkyl phosphorotetrathioates may be characterized as their mercuric salts.[1255] Triethyl phosphorotetrathioate is formed from tetraphosphorus decasulphide and triethyl trithio-orthoformate[1465]:

$$P_2S_5 + 3HC(SEt)_3 \rightarrow 2(EtS)_3PS + 3EtSCHS$$

Symmetrical trialkyl and triaryl phosphorotetrathioates are readily obtained by the action of sodium mercaptide on thiophosphoryl chloride.[1079, 1148, 1299, 2061]

*S,S,S*-Phosphorotrithioates, $(RS)_3PO$, may be prepared by oxidation of phosphorotrithioites first with air at 230°F. to about 80% completion and then with hydrogen peroxide,[1124] or from sodium mercaptide and phosphoryl chloride.[2061] Comparative rates of hydrolysis of $(EtO)_3PO$ and $(EtS)_3PO$ are given by Thain.[1125] Molar magnetic rotations of the lower trialkyl tri- and tetra-thiophosphates are recorded.[2061]

The reaction of lower sulphides of phosphorus with alcohols was studied by Kabachnik[635]; the isolated products testify to the complex nature of the reactions and are indicated below:

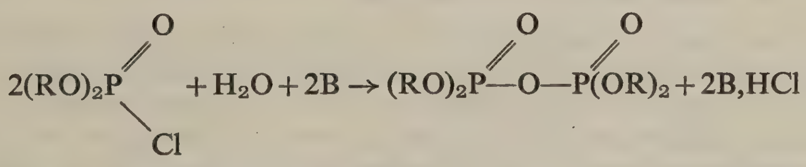
| Phosphorus sulphide | Reaction products with alcohol |
|---|---|
| $P_4S_7$ | $(RO_2PSH$, $(RO)_2PS_2H$, $(RO)_2PS.SR$, $H_2S$, P, $PH_3$ |
| '$P_4S_6$' | $(RO)_2PSH$, $(RO)_2PS.SR$, $H_2S$ |
| $P_4S_5$ | $(RO)_2PSH$, $(RO)_2PS.SR$ |
| '$P_4S_4$' | $(RO)_2PSH$, $(RO)_2PS.SR$, lower yields than from $P_4S_7$, $P_4S_6$ |

## DERIVATIVES OF PYROPHOSPHORIC ACID, THEIR SULPHUR AND SELENIUM ANALOGUES, AND HIGHER CONDENSED ACIDS

### Preparation of Pyrophosphates

#### CONDENSATION OF PHOSPHORYL HALIDATES

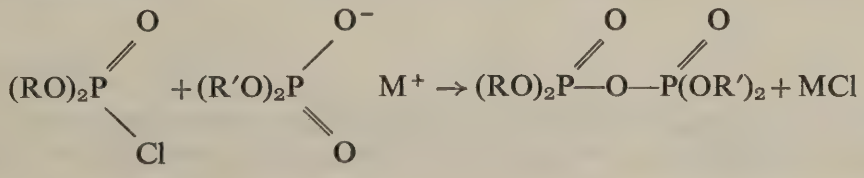
One of the simplest ways of obtaining symmetrical tetraesters of pyrophosphoric acid is the controlled hydrolysis of a dialkyl/aryl phosphorochloridate, generally in the presence of a base such as pyridine or sodium hydroxide[1482, 1532, 1549, 1551, 1554]:



$$\mathrm{2(RO)_2\underset{Cl}{\overset{O}{P}} + H_2O + 2B \rightarrow (RO)_2\overset{O}{P}{-}O{-}\overset{O}{P}(OR)_2 + 2B,HCl}$$

The reaction fails with dialkyl phosphorofluoridates.[1551]

A closely related reaction, which provides a route to unsymmetrical pyrophosphates[1534, 1589, 1599] is the reaction of a phosphorochloridate with the salt of a secondary phosphate[1230, 1415, 1548, 1550]:

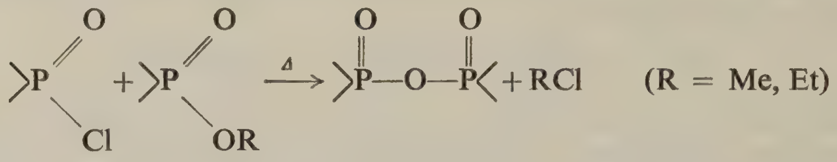


$$\mathrm{(RO)_2\underset{Cl}{\overset{O}{P}} + (R'O)_2\underset{O}{\overset{O^-}{P}}\ M^+ \rightarrow (RO)_2\overset{O}{P}{-}O{-}\overset{O}{P}(OR')_2 + MCl}$$

The formation of pyrophosphates by reaction of dialkyl phosphites with a polyhalogenated methane derivative and a base[673, 1089] probably proceeds via intermediate formation of halidate and acid salt:

$$2(RO)_2POH + 2CCl_4 + 2NaOH \rightarrow (RO)_4P_2O_3 + 2CHCl_3 + H_2O + 2NaCl$$

Pyrophosphates are formed by the thermal elimination of alkyl chloride between a molecule of a phosphorochloridate and a molecule of a tertiary phosphate ester. By using monofunctional reagents good yields of pyrophosphates may be obtained.[1533, 1536] The mechanisms and scope of the reaction are discussed by Stölzer and Simon [1487]:



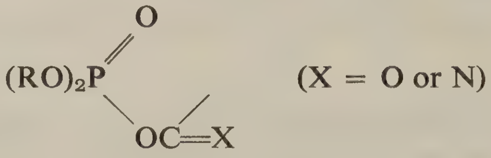
In its simplest form, the reaction of phosphoryl chloride with triethyl phosphate, the reaction was used by Schrader for the preparation of an insecticide formulated as hexaethyl tetraphosphate (Bladan):

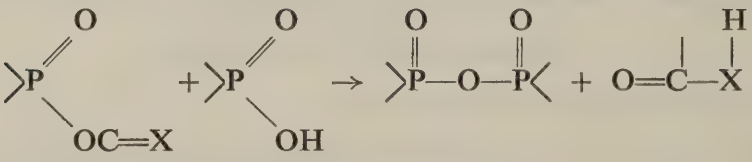
$$POCl_3 + 3(EtO)_3PO \rightarrow OP[OPO(OEt)_2]_3$$

More recent work on this reaction indicates the product to be a mixture of condensed phosphates of which the component with greatest physiological activity, tetraethyl pyrophosphate (TEPP), constitutes some 10–15%.[1531] Products which contain higher proportions of TEPP (up to about 40%) may be obtained using a higher ratio of phosphate to phosphoryl chloride.[1536, 1552]

### CONDENSATIONS INVOLVING REACTIVE PHOSPHATE ESTER INTERMEDIATES

Many elegant pyrophosphate syntheses involve condensation of phosphoric acid or its esters with reactive intermediates, or in some cases isolable compounds of the type:

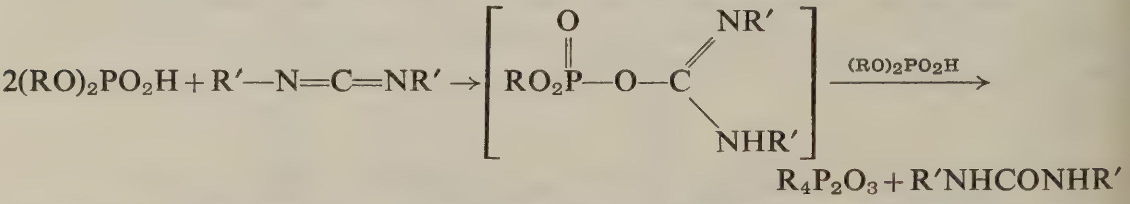




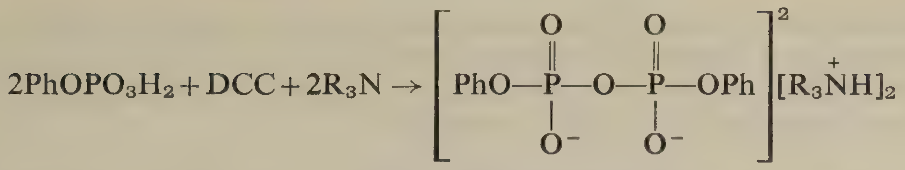
The principal examples are discussed below:

#### *Use of Carbodi-imides and Related Compounds*

Dialkyl and diaryl phosphates react readily with carbodi-imides (generally, di*cyclo*hexyl carbodi-imide (DCC) has been used) at room temperature to form a symmetrical tetraester of pyrophosphoric acid and a urea derivative.[1123, 1382, 1384] Salts of dialkyl phosphates and weak bases such as pyridine behave similarly, but salts of strong bases such as triethylamine do not react.[1383, 1429] The reaction is thought to proceed via the formation of an intermediate isourea phosphate[1382]:

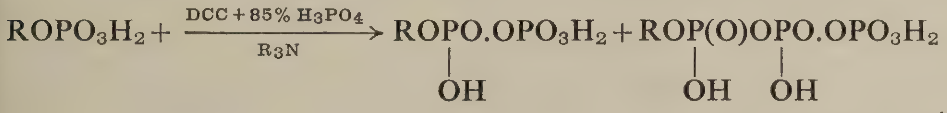


Monoalkyl phosphates[1382] or their monobasic salts with strong tertiary organic bases such as tributylamine[1383] yield *P*,*P*′-disubstituted pyrophosphates, e.g.,



$$2PhOPO_3H_2 + DCC + 2R_3N \rightarrow \left[ PhO-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-OPh \right]^{2}[R_3\overset{+}{N}H]_2$$

In the nucleotide field Khorana and co-workers have prepared mixtures of nucleotide di- and tri-phosphates by the reaction of nucleotide-5′-phosphates with an excess of phosphoric acid and DCC[1561-2]:

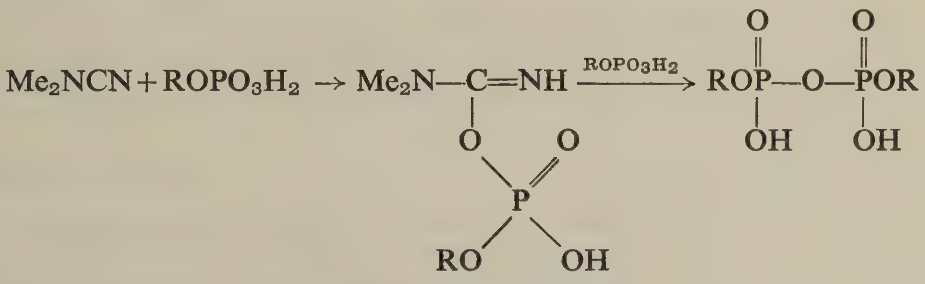


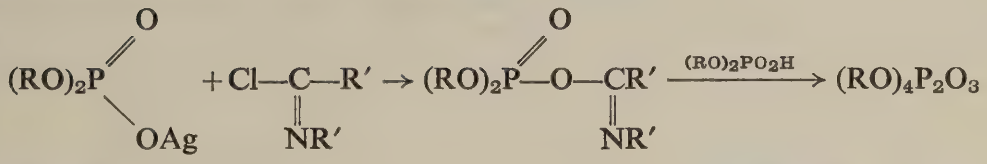
$$ROPO_3H_2 + \xrightarrow[R_3N]{DCC + 85\%\ H_3PO_4} RO\underset{\underset{OH}{|}}{P}O.OPO_3H_2 + RO\underset{\underset{OH}{|}}{P}(O)O\underset{\underset{OH}{|}}{P}O.OPO_3H_2$$

(as $R_3N$ salts)

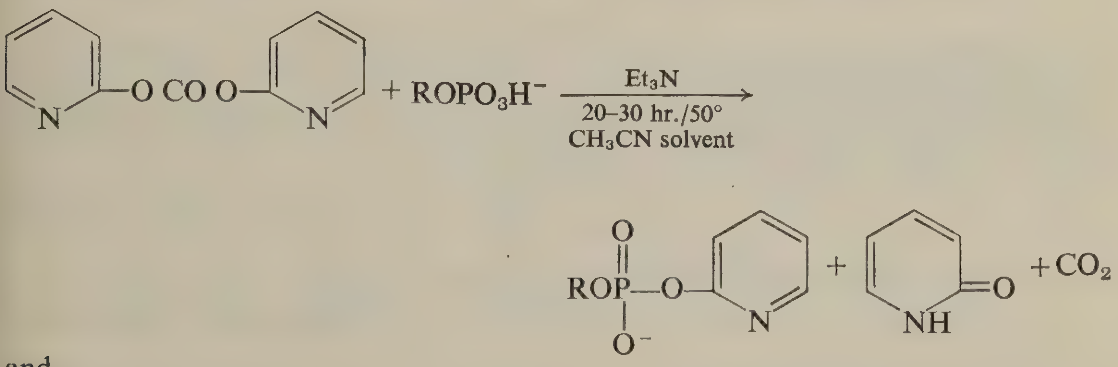
### *Imidoyl Phosphates and α-Pyridyl Phosphates*

Analogous to the hypothetical intermediates formed in carbodi-imide condensations are the imidoyl phosphates.[1123] Such compounds may be prepared by the Beckmann rearrangement of oximes in the presence of a phosphate or by the action of silver or tertiary amine salts of dialkyl phosphates with an imidoyl chloride.[1123, 1563] They can be prepared as reactive intermediates by the action of dimethyl cyanamide ($Me_2NCN$),[1535] or keten imides ($R{-}CH{=}C{=}NR_2$)[1377] with a dialkyl phosphate and by reaction of trichloroacetonitrile with an acid phosphate.[1438-9] They react with acid phosphates to form pyrophosphate derivatives:

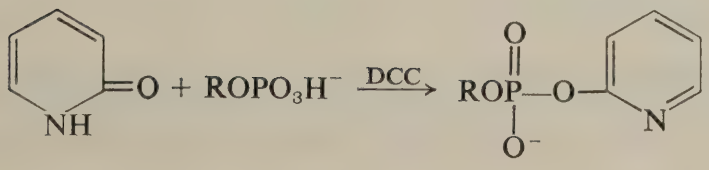




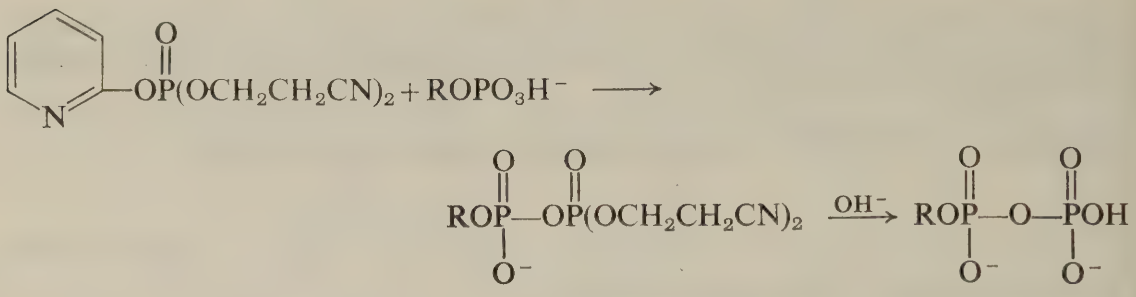
Closely related to imidoyl phosphates are the α-pyridyl phosphates, which may be obtained by reaction of a monoalkyl or aryl acid phosphate salt with di-α-pyridyl carbonate or the corresponding acid with α-hydroxypyridine and DCC[1623]:



and

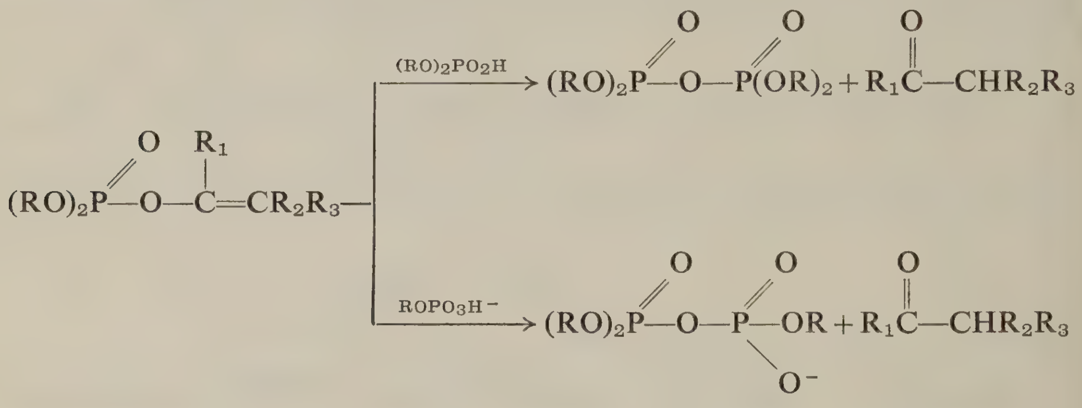


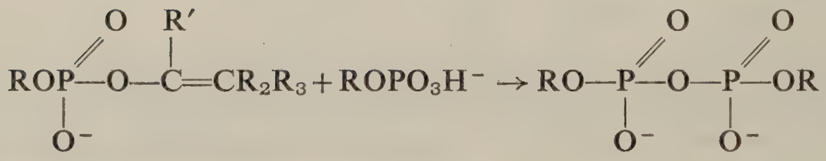
They react with phosphoric acid monoesters, giving symmetrical diesters of pyrophosphates, with alcohols giving phosphoric acid diesters, and with amines to give phosphoric acid ester amides. Monoesters of pyrophosphoric acid can be prepared using bis(2-cyanoethyl)-α-pyridyl phosphate[1544]:



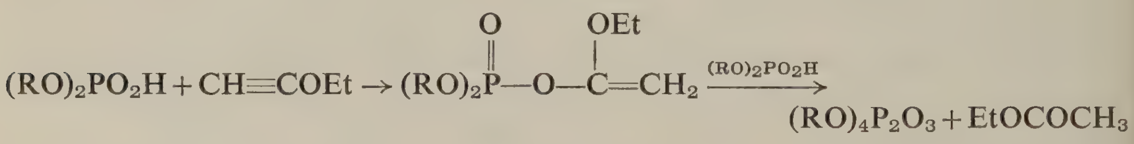
### *Vinyl Phosphates*

Vinyl esters of phosphoric acid react with di- and mono-substituted esters of phosphoric acid, when a carbonyl compound corresponding to the vinyl ester is eliminated and a pyrophosphate is formed. Tetra-,[1020] tri-,[1440, 1539] and symmetrical di-pyrophosphate esters[1547] may be prepared in this way:





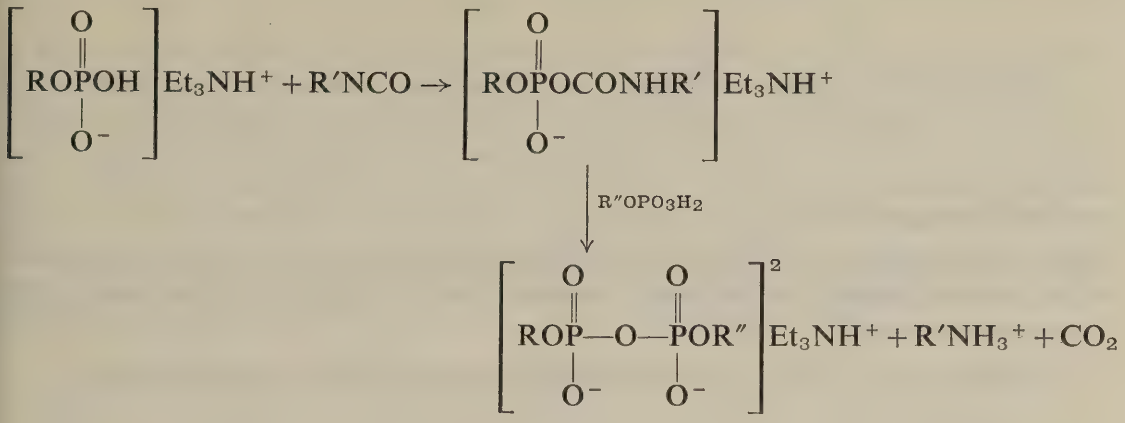
Symmetrical tetra-alkyl pyrophosphates may be prepared by the condensation of secondary phosphates in the presence of ethoxyacetylene[1546]; the intermediate 1-ethoxyvinyl phosphates can be obtained by reaction of dialkyl phosphates and ethoxyacetylene in the presence of a mercuric salt[1505]:

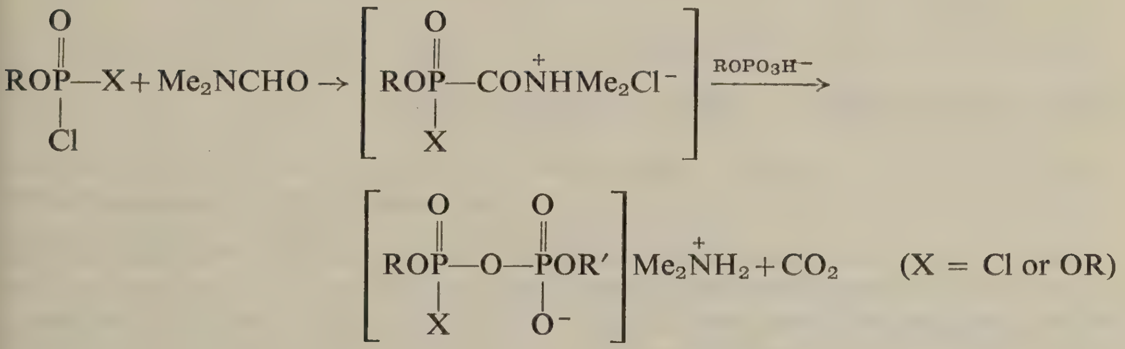


$$(RO)_2PO_2H + CH{\equiv}COEt \rightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}O{-}\overset{\overset{\displaystyle OEt}{|}}{C}{=}CH_2 \xrightarrow{(RO)_2PO_2H} (RO)_4P_2O_3 + EtOCOCH_3$$

### *Carbamoyl Phosphates*

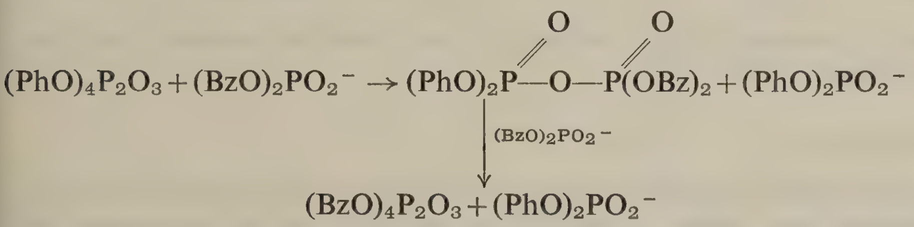
Monobasic anions of phosphoric acid or its monoesters react with organic isocyanates, giving anhydrides of phosphoric acid and carbamic acid which react with more phosphoric acid or ester to form phosphoric acid anhydrides.[1447] Similar compounds are formed by reaction of phosphorohalidate with dimethylformamide[1538]:





### BY EXCHANGE REACTIONS

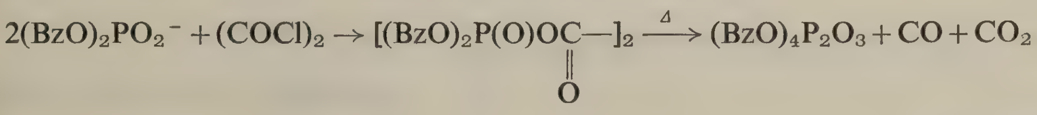
The formation of pyrophosphates by exchange reactions has been studied largely by Todd and his co-workers. Highly reactive pyrophosphates such as tetraphenyl pyrophosphate readily undergo exchange with dialkyl phosphates in the presence of a base to form tetra-alkyl pyrophosphate and diphenyl phosphate[1415, 1548]; thus tetrabenzyl pyrophosphate may be prepared by reaction with dibenzyl phosphate:



Such exchange reactions always occur so as to produce the less reactive pyrophosphate, i.e., the salt of the stronger phosphoric acid. Similar exchange reactions take place between secondary phosphates and anhydrides, such as trifluoroacetic acid anhydride[1429, 1548] or tetraethyl pyrophosphite,[1545] and acid chlorides such as aromatic sulphonyl chlorides,[1386, 1393, 1548, 1574] thionyl chloride,[1415] and diethyl phosphorochloridite,[1542] to yield the symmetrical pyrophosphate ester:

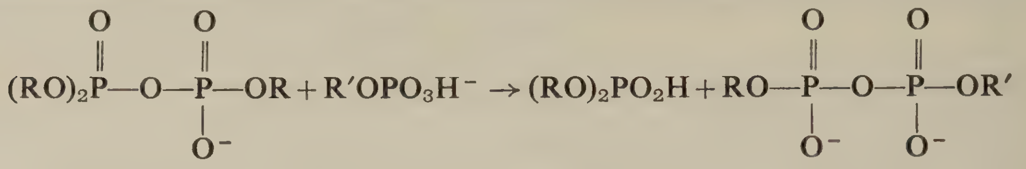
$$2(RO)_2PO_2^- + ArSO_2Cl \rightarrow (RO)_4P_2O_3 + Cl^- + ArSO_3^-$$
$$2(EtO)_2PO_2H + (EtO)_2P{-}O{-}P(OEt)_2 \rightarrow (EtO)_4P_2O_3 + 2(EtO)_2POH$$

Oxalyl chloride and dibenzyl phosphate react to form a crystalline mixed anhydride which decomposes on heating to tetrabenzyl pyrophosphate[1415]:



$$2(BzO)_2PO_2^- + (COCl)_2 \rightarrow [(BzO)_2P(O)O\underset{\underset{O}{\|}}{C}{-}]_2 \xrightarrow{\Delta} (BzO)_4P_2O_3 + CO + CO_2$$

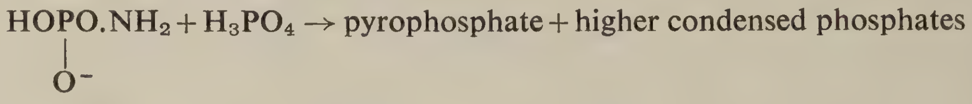
*P,P′-unsym*-Pyrophosphate diesters can be prepared by exchange reactions between salts of triesters of pyrophosphoric acid and monobasic primary phosphate[1440]:



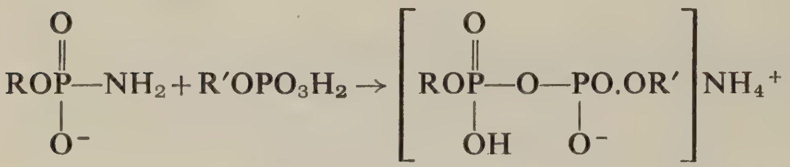
$$\mathrm{(RO)_2\overset{\overset{O}{\|}}{P}{-}O{-}\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}{-}OR + R'OPO_3H^- \rightarrow (RO)_2PO_2H + RO{-}\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}{-}OR'}$$

FROM PHOSPHORAMIDATES

Salts of phosphoramidic acid and alkyl phosphoramidic acids, but not phosphoramidic diesters themselves, are weak phosphorylating agents for phosphoric acid in aqueous solution[1568-71, 2066, 2068]:



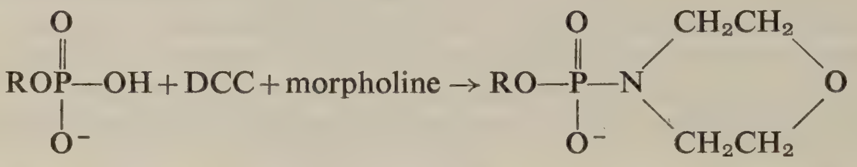
$$\mathrm{HO\underset{\underset{O^-}{|}}{P}O.NH_2 + H_3PO_4 \rightarrow}\text{ pyrophosphate + higher condensed phosphates}$$



$$\mathrm{RO\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}{-}NH_2 + R'OPO_3H_2 \rightarrow \left[RO\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{O^-}{|}}{P}O.OR'\right]NH_4^+}$$

(R = benzyl, R′ = adenosine-5-)[1570]

The early work using phosphoramidates has been considerably developed by the use of *O*-alkyl *N*-substituted phosphoramidic acids derived from amines such as aniline, benzylamine, and morpholine[1557-8, 1567, 1572] and of *O*-alkyl phosphoroimidazolides.[1200, 1595] A useful introduction has been the direct formation of *O*-alkyl phosphoramidic acids, particularly nucleotide phosphoramidates, by reaction of a monoester of phosphoric acid with an excess of di*cyclo*hexyl carbodi-imide and an amine such as morpholine[1557-8, 1567, 1573]:



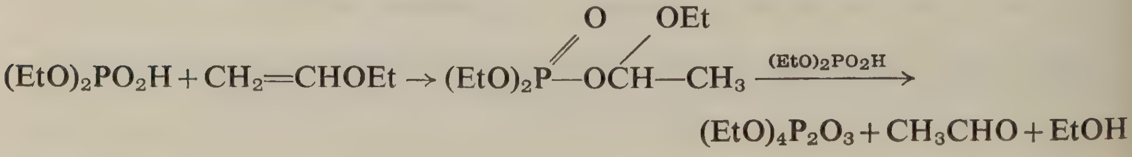
The mechanism of pyrophosphate formation from phosphoramidates has been investigated by Hamer.[2420, 2421]

MISCELLANEOUS METHODS

Tetraethyl pyrophosphate has been obtained by the following methods: action of phosphorus pentoxide on diethyl ether[1498]; action of salts of carboxylic and carbonic acids on diethyl phosphorochloridate[1578, 1608]; action of silver nitrate,[1541] silver carbonate[1608] or lead carbonate[1603] on diethyl phosphorochloridite; oxidation of diethyl phosphite with nitrosyl chloride in the presence of pyridine[1077, 1542]; oxidation of tetraethyl pyrophosphite or $(EtO)_2PO.OP(OEt)_2$ with dinitrogen tetroxide[862]; heating a mixture of diethyl phosphate and triethyl phosphate with copper bronze[1531]; action of ethyl vinyl ether on diethyl phosphate[1545]; and the reaction of phosphoryl chloride with less than the calculated amount of ethanol[1592]:

$$\mathrm{2(EtO)_2PCl + 2AgNO_2 \rightarrow (EtO)_4P_2O_3 + 2AgCl + N_2 + N_2O}$$

$$\mathrm{2(EtO)_2PO.H + 2NOCl \xrightarrow{pyridine} (EtO)_4P_2O_3 + 2HCl + N_2O}$$



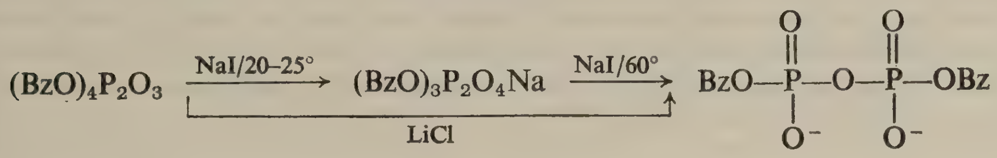
Silver salts of pyrophosphoric acid[1,1531] or its partial esters react readily with alkyl iodides giving the tetrasubstituted pyrophosphate[1537,1576]:

$$Ag_4P_2O_7 + 4EtI \rightarrow (EtO)_4P_2O_3 + 4AgI$$

A mixture of *P,P*-diethyl and *P,P′*-diethyl pyrophosphates is reported to be formed by the action of an excess of ethanol on phosphorus pentoxide.[1577]

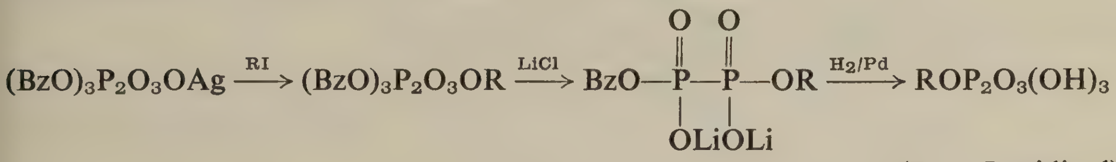
Dealkylation, usually debenzylation, reactions have been fairly widely used in the pyrophosphate field to prepare esters of mono-,[1576,1589] tri- and *P,P*-disubstituted pyrophosphates. Benzyl groups can be removed from benzyl-substituted pyrophosphate esters by metal salts such as lithium chloride,[1576] sodium iodide[1537] or lithium thiocyanate, by tertiary amines and by phenolysis[1589,1599] to give the *P,P′*-diester from which any residual benzyl groups can be removed by hydrogenation over palladium catalyst[1589,1599]:

$$(Bu_3NH)_2{}^+HPO_4{}^- \xrightarrow{DCC} (Bu_3NH)_3P_3O_9$$



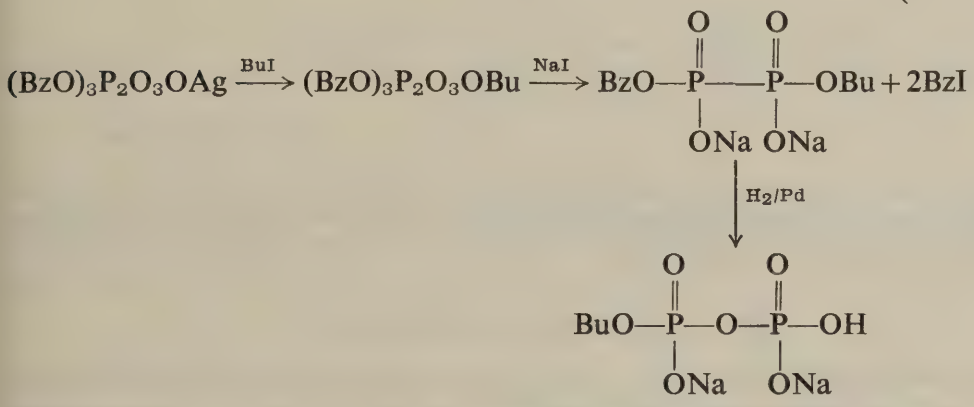
$$(BzO)_4P_2O_3 \xrightarrow{NaI/20\text{–}25^\circ} (BzO)_3P_2O_4Na \xrightarrow{NaI/60^\circ} BzO\text{—}\overset{O}{\underset{O^-}{P}}\text{—}O\text{—}\overset{O}{\underset{O^-}{P}}\text{—}OBz \qquad (BzO)_4P_2O_3 \xrightarrow{LiCl} BzO\text{—}\overset{O}{\underset{O^-}{P}}\text{—}O\text{—}\overset{O}{\underset{O^-}{P}}\text{—}OBz$$

The general procedures applicable in this field are illustrated by the formation of uridine diphosphate,[1576] *P*-butyl-*P′*-benzyl pyrophosphate[1537] and monobutyl pyrophosphate[1537] from silver tribenzyl pyrophosphate:



$$(BzO)_3P_2O_3OAg \xrightarrow{RI} (BzO)_3P_2O_3OR \xrightarrow{LiCl} BzO\text{—}\overset{O}{\underset{OLi}{P}}\text{—}\overset{O}{\underset{OLi}{P}}\text{—}OR \xrightarrow{H_2/Pd} ROP_2O_3(OH)_3$$

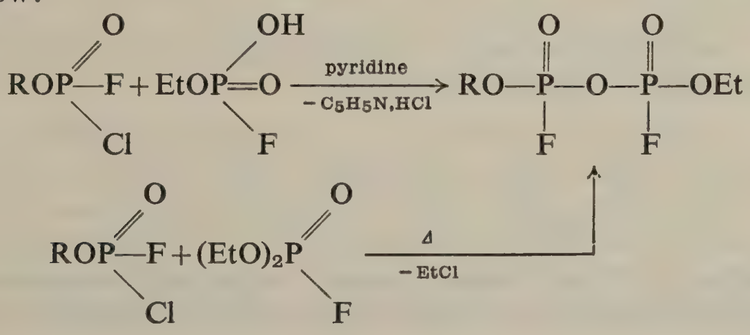
(R = 5-uridinyl)



$$(BzO)_3P_2O_3OAg \xrightarrow{BuI} (BzO)_3P_2O_3OBu \xrightarrow{NaI} BzO\text{—}\overset{O}{\underset{ONa}{P}}\text{——}\overset{O}{\underset{ONa}{P}}\text{—}OBu + 2BzI \xrightarrow{H_2/Pd} BuO\text{—}\overset{O}{\underset{ONa}{P}}\text{—}O\text{—}\overset{O}{\underset{ONa}{P}}\text{—}OH$$

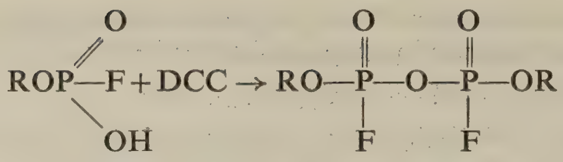
## Esters of Fluorodiphosphoric Acids

As a consequence of the high stability of the P–F bond, esters of *P,P′*-difluorodiphosphoric acid may be obtained by conventional synthesis from suitable fluoro-substituted phosphoric acid derivatives.[1136,1483,1487–8] Typical reactions are indicated below:

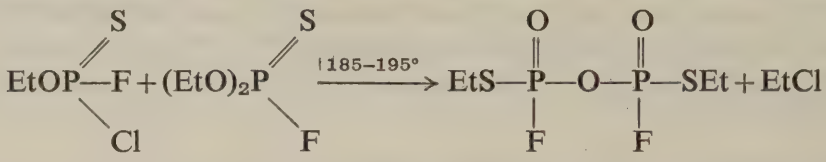


$$ROP\overset{O}{\underset{Cl}{\text{—}}}F + EtOP\overset{OH}{\underset{F}{=}}O \xrightarrow[-C_5H_5N,HCl]{pyridine} RO\text{—}\overset{O}{\underset{F}{P}}\text{—}O\text{—}\overset{O}{\underset{F}{P}}\text{—}OEt$$

$$ROP\overset{O}{\underset{Cl}{\text{—}}}F + (EtO)_2P\overset{O}{\underset{F}{}} \xrightarrow[-EtCl]{\Delta} RO\text{—}\overset{O}{\underset{F}{P}}\text{—}O\text{—}\overset{O}{\underset{F}{P}}\text{—}OEt$$

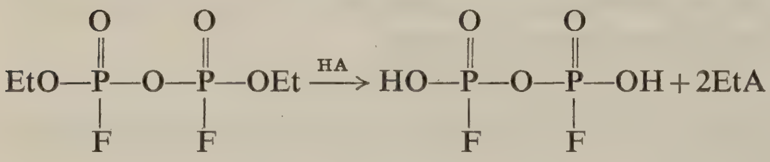


The thermal reaction of *O*-ethyl phosphorochloridofluoridothionate with *O*,*O*-diethyl phosphorofluoridate occurs with rearrangement of ethyl groups from oxygen to sulphur to form *sym*-*S*,*S*-diethyl difluorodithiopyrophosphate[1487]:



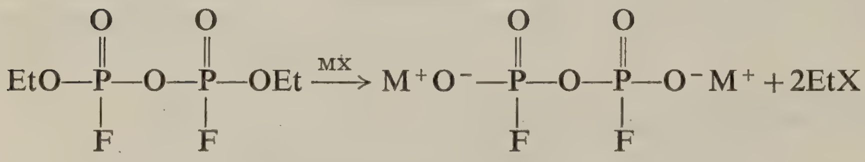
Compounds having a fluorine atom and an alkoxyl group attached to the same phosphorus atom undergo facile dealkylation with organic acids giving the acid ester and a fluorophosphoric acid. Dealkylation by metal salts, tertiary amines or thiourea yields the metal, quaternary ammonium or alkyl isothiouronium salt of the fluorophosphoric acid respectively[1485–7]:

$$\mathrm{EtOPOF_2 + R_3N \rightarrow [R_3\overset{+}{N}H][PO_2F_2]^-}$$



$$\mathrm{EtO{-}\overset{O}{\underset{F}{P}}{-}O{-}\overset{O}{\underset{F}{P}}{-}OEt \xrightarrow{HA} HO{-}\overset{O}{\underset{F}{P}}{-}O{-}\overset{O}{\underset{F}{P}}{-}OH + 2EtA}$$

(HA = phenol or $\mathrm{RCO_2H}$)



$$\mathrm{EtO{-}\overset{O}{\underset{F}{P}}{-}O{-}\overset{O}{\underset{F}{P}}{-}OEt \xrightarrow{MX} M^+O^-{-}\overset{O}{\underset{F}{P}}{-}O{-}\overset{O}{\underset{F}{P}}{-}O^-M^+ + 2EtX}$$

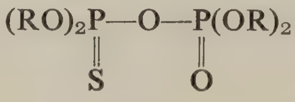
(X = I, Cl, OAc, $\mathrm{NO_3}$)

Fluorophosphoric acid and *sym*-difluoropyrophosphoric acid can also be formed by hydrogenolysis of diphenyl phosphorofluoridate and *P*,*P*′-diphenyl-*P*,*P*′-difluoropyrophosphoric acid, respectively.[1136]

### Thio- and Seleno-pyrophosphates

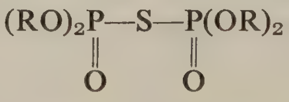
Known characterized derivatives of thiopyrophosphoric acids are limited almost entirely to fully esterified lower *O*-alkyl esters of mono-, di-, and tri-thiopyrophosphoric acid and to various ester amides and amides which are of considerable interest as potential insecticides. Generally the compounds exhibit a moderately high anticholinesterase action[1078–9, 1132, 1594, 1612]; they are less toxic and more stable to hydrolysis than the corresponding pyrophosphate esters. Preparation of thio- and seleno-pyrophosphates has been reviewed by Schrader *et al.*[1078] and by McIvor *et al.*[1079]

Tetra-alkyl monothiopyrophosphates could conceivably exist in two isomeric forms, a thiono form **I**, and a thiolo form **II**.



$$\mathrm{(RO)_2\underset{S}{P}{-}O{-}\underset{O}{P}(OR)_2}$$

**I**



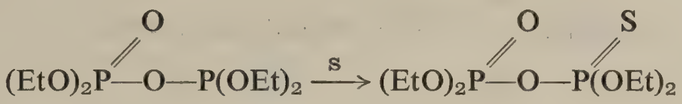
$$\mathrm{(RO)_2\underset{O}{P}{-}S{-}\underset{O}{P}(OR)_2}$$

**II**

Raman,[1585] infra-red,[1079] and nuclear magnetic resonance[1579] spectra show that the compounds always exist in the thiono form (I) even when the method of preparation, e.g., oxidation of tetraethyl thiopyrophosphite, $(EtO)_2P{-}S{-}P(OEt)_2$,[634] might reasonably be expected to yield the thiolo form. Tetraethyl selenopyrophosphate,[1581] like the sulphur compound, exists in the selenono rather than a selenolo form.[354,1579]

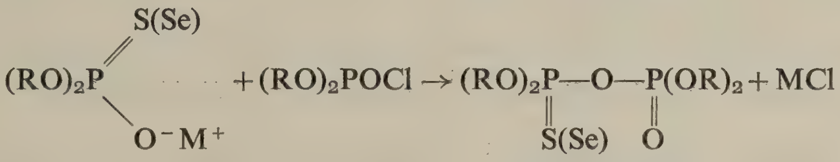
PREPARATION

Tetraethyl thionopyrophosphate was first prepared by Arbuzov in 1931 by the addition of sulphur to tetraethyl phosphorous phosphoric anhydride[1584]:

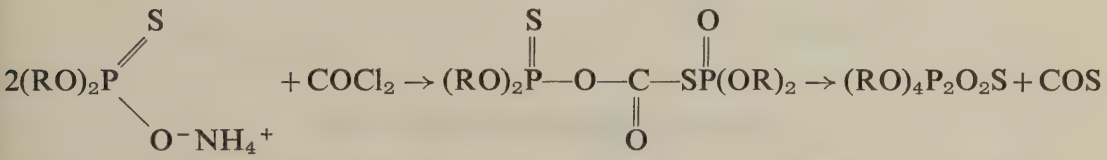


$$(EtO)_2\overset{O}{P}—O—P(OEt)_2 \xrightarrow{S} (EtO)_2\overset{O}{P}—O—\overset{S}{P}(OEt)_2$$

Tetraesters of monothio- and monoseleno-pyrophosphoric acids may be obtained from a dialkyl phosphorothioic acid or dialkyl phosphoroselenoic acid, respectively, by reaction with a dialkyl phosphorochloridate and tertiary base,[1132,1594] from a salt of the acid and phosphorochloridate,[1132,1582–3,1602] or by the action of hydrogen sulphide on a phosphorochloridate.[1582] Salts of dialkyl phosphorothioic acids react with carbonyl chloride,[1592] thiocarbonyl chloride[1592] or oxalyl chloride,[1602] giving monothiopyrophosphates:

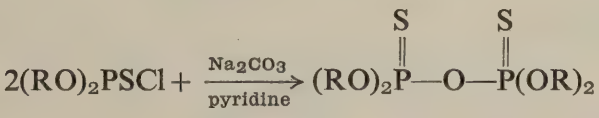


$$(RO)_2\overset{S(Se)}{\underset{O^-M^+}{P}} + (RO)_2POCl \rightarrow (RO)_2\underset{S(Se)}{P}—O—\underset{O}{P}(OR)_2 + MCl$$



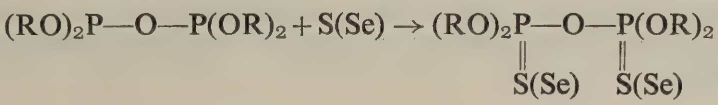
$$2(RO)_2\overset{S}{\underset{O^-NH_4^+}{P}} + COCl_2 \rightarrow (RO)_2\overset{S}{P}—O—\underset{O}{C}—S\overset{O}{P}(OR)_2 \rightarrow (RO)_4P_2O_2S + COS$$

Dithio-compounds are readily prepared by careful hydrolysis of *O,O*-dialkyl phosphorochloridothionates by water and tertiary base or better by the action of an alkali metal carbonate with pyridine catalyst[1593–4]:



$$2(RO)_2PSCl + \xrightarrow[\text{pyridine}]{Na_2CO_3} (RO)_2\overset{S}{P}—O—\overset{S}{P}(OR)_2$$

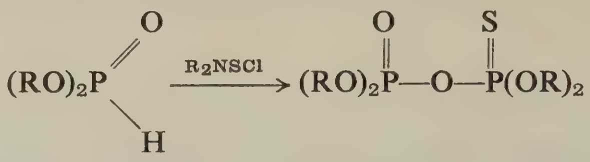
Tetra-alkyl dithiopyrophosphates or tetra-alkyl diselenopyrophosphates can be formed by the addition of sulphur or selenium to tetra-alkyl pyrophosphite[1602]:

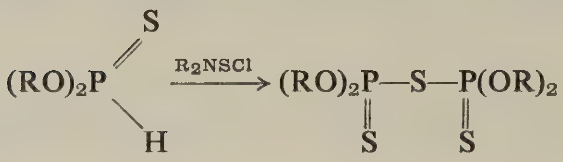


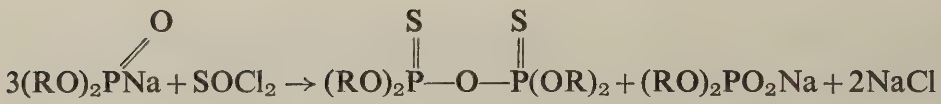
$$(RO)_2P—O—P(OR)_2 + S(Se) \rightarrow (RO)_2\underset{S(Se)}{P}—O—\underset{S(Se)}{P}(OR)_2$$

A number of reactions of dialkyl phosphites result in the formation of thiopyrophosphate, e.g., reaction of $(RO)_2POH$ with sulphur dichloride[709,710,1078] and pyridine or with $Me_2NSCl$.[710,1078] Dithiopyrophosphates result from the reaction of a sodium dialkyl phosphite with thionyl chloride.[1078] Trithiopyrophosphates are formed from *O,O*-dialkyl thiophosphites and amine sulphenyl chloride[1078,1099,1100];

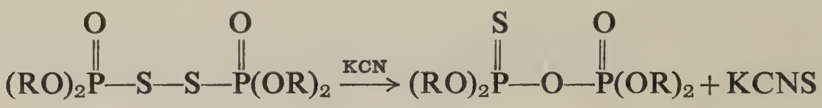
physical properties of a number of these compounds are listed by Almasi and Hantz[1099]:



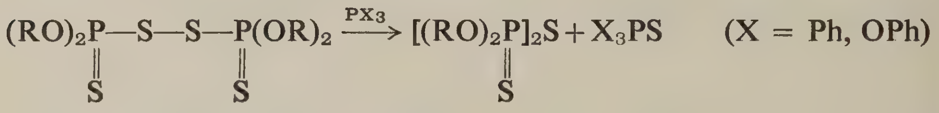




Bis-dialkoxyphosphoryl disulphides and bis-dialkoxythiophosphoryl disulphides may be reduced by potassium cyanide,[1078] triphenylphosphine or triphenyl phosphite[1603] (contrast the action of trialkyl phosphites with $(RO)_2P_2S_4$[1605] and $[(RO)_2PO]Se_2$,[1002] p. 1010) giving mono and trithiopyrophosphates, respectively:



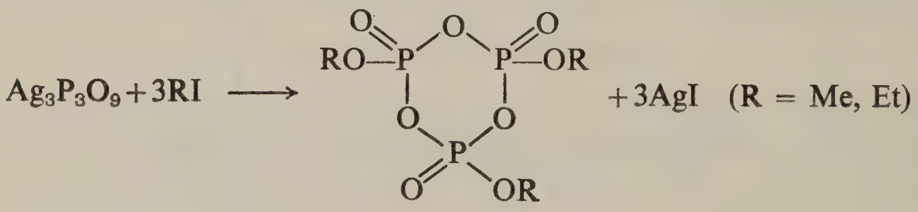
$$(RO)_2\overset{O}{\overset{\|}{P}}-S-S-\overset{O}{\overset{\|}{P}}(OR)_2 \xrightarrow{KCN} (RO)_2\overset{S}{\overset{\|}{P}}-O-\overset{O}{\overset{\|}{P}}(OR)_2+KCNS$$



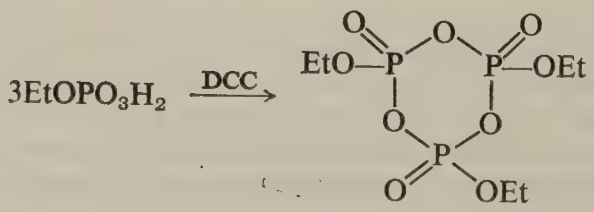
$$(RO)_2\underset{S}{\underset{\|}{P}}-S-S-\underset{S}{\underset{\|}{P}}(OR)_2 \xrightarrow{PX_3} [(RO)_2\underset{S}{\underset{\|}{P}}]_2S+X_3PS \qquad (X = Ph, OPh)$$

## Esters of Trimetaphosphoric Acid

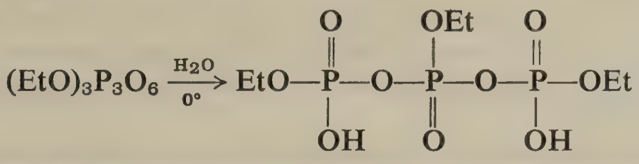
Silver trimetaphosphate and methyl or ethyl iodide react in acetonitrile solution giving the corresponding trialkyl trimetaphosphates[1409]:



A novel reaction used to prepare triethyl trimetaphosphate and less pure samples of the tris(2-cyanoethyl) and tribenzyl esters is the condensation of a monoalkyl phosphate with an excess of di*cyclo*hexyl carbodi-imide in dry dioxan[1386]; in a similar reaction bis(tributylammonium) phosphate condenses to tributyl ammonium trimetaphosphate:



Triethyl trimetaphosphate is hydrolyzed almost instantly at 0° in water to form the linear triethyl tripolyphosphate (cf. ref. 1386)

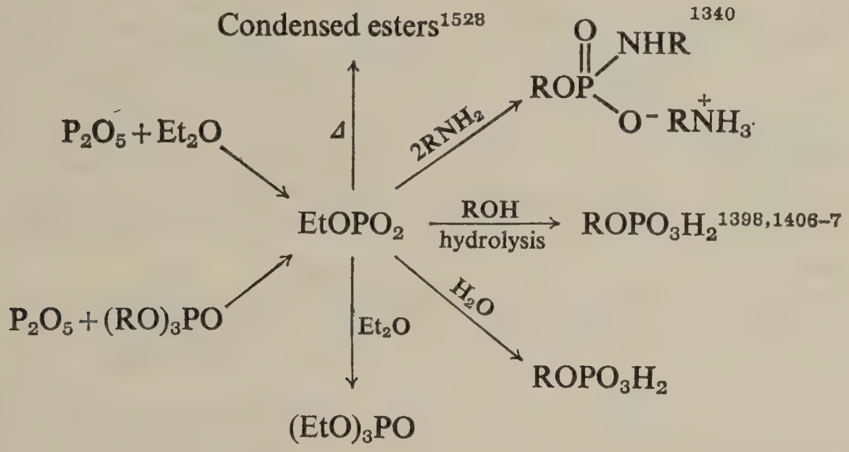


$$(EtO)_3P_3O_6 \xrightarrow[0^\circ]{H_2O} EtO-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{O}{\underset{\|}{\overset{OEt}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-OEt$$

Methanolysis of the trimethyl ester (prepared by the silver salt method) is stated to yield 50% tetramethyl pyrophosphate and 35% monomethyl phosphate[1409]; in contrast, methanolysis of the triethyl ester (prepared by the DCC method) gives 89–90% ethyl methyl phosphoric acid.[1386] Aniline and the triethyl ester form anilinium *O*-ethyl-*N*-phenyl phosphoramidate.[1386]

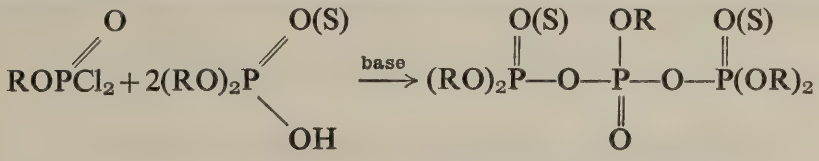
### 'ETHYL METAPHOSPHATE'

The chloroform-soluble ethyl metaphosphate $(EtOPO_2)_n$ which may be prepared, following Langheld,[1398, 1405] by reaction of phosphorus pentoxide with diethyl ether in chloroform solution, has been investigated by several groups of workers. The infra-red spectrum bears some resemblance to that of triethyl trimetaphosphate,[1409] and the nuclear magnetic resonance spectrum[1399–1400] and chromatographic analysis[1401] indicate the substance to consist of a number of ethylated condensed acids of phosphorus. Thilo *et al.* conclude from their chromatographic analysis[1401] that the Langheld ester does not consist of a mixture of tetraethyl tetrametaphosphate and tetraethyl *iso*tetrametaphosphate, as was assumed previously by Rätz and Thilo,[1587] on the basis of hydrolysis and ammonolysis. Formation and reactions of 'ethyl metaphosphate' are indicated below:

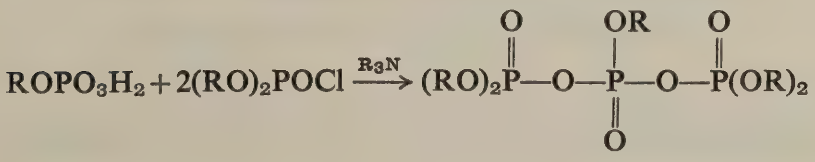


## Esters of Triphosphoric Acid

Pentaesters of triphosphoric acid and dithiotriphosphoric acids have generally been obtained by interaction of the appropriate phosphorodichloridate with the salt of a dialkyl-phosphoric or phosphorothioic acid,[1132, 1550, 1553, 1588] or from a phosphoric acid monoester and dialkyl phosphorochloridate generally in the presence of a tertiary base.[1550, 1553] Few compounds other than lower alkyl esters are known:



$$ROPCl_2{=}O + 2(RO)_2P({=}O(S))OH \xrightarrow{base} (RO)_2\overset{O(S)}{\overset{\|}{P}}-O-\underset{O}{\underset{\|}{\overset{OR}{P}}}-O-\overset{O(S)}{\overset{\|}{P}}(OR)_2$$

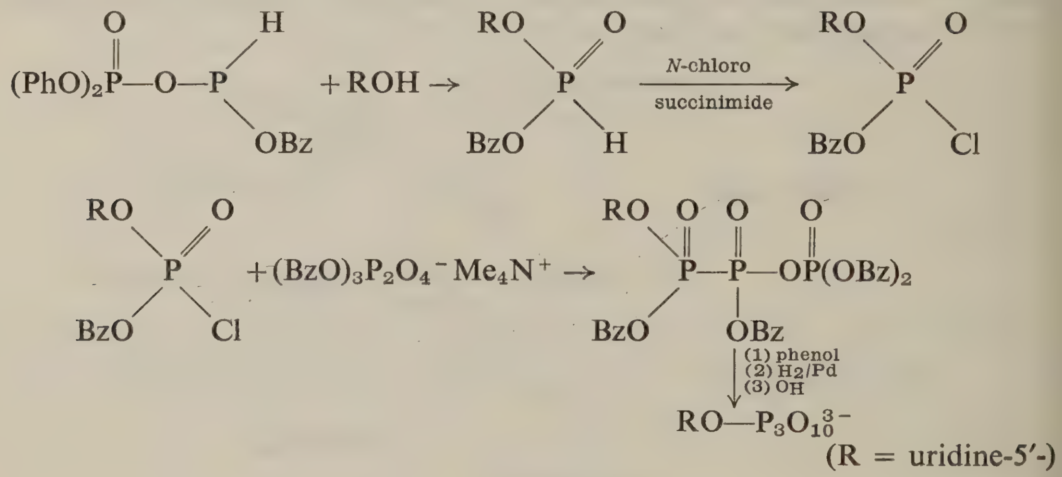


$$ROPO_3H_2 + 2(RO)_2POCl \xrightarrow{R_3N} (RO)_2\overset{O}{\overset{\|}{P}}-O-\underset{O}{\underset{\|}{\overset{OR}{P}}}-O-\overset{O}{\overset{\|}{P}}(OR)_2$$

Pentaethyl triphosphate prepared by the classical technique from pentasilver triphosphate and ethyl iodide[1179,1601] consists of a mixture of compounds.[1408] Hydrolysis gives $(EtO)_2PO_2H$ and $EtOPO_3H_2$ in close to the theoretical 2:1 ratio; ammonolysis gives a 2:1 mixture of ammonium phosphoramidate and ammonium diethyl phosphate.[1601] Hydrolysis data for pentaethyl triphosphate are given by Simon and Stölzer.[1550]

The patent literature contains a number of claims for the formation of penta-alkyl triphosphates and hexa-alkyl tetraphosphates which, in view of the ready reorganization of polyphosphate esters[1408] and the techniques of preparation given are almost certainly mixtures of several condensed esters (cf. ref. 1590). Such methods are the thermal reaction of phosphoryl chloride with triethyl phosphate,[1536] the reaction of phosphorus pentoxide with diethyl ether[1528] or with phenol,[1179] the direct reaction of alcohols with phosphoryl chloride[1591] and the reaction of phosphorus pentoxide with triethyl phosphate.[1339] The 'pentaethyl triphosphate' prepared by the last method yields mainly diethyl and monoethyl phosphates on hydrolysis, but not in the calculated 2:1 ratio.[1601]

Adinosine-5′-triphosphate[1596] and uridine-5′-triphosphate,[1589] identical with the naturally occurring compounds, have been prepared by Todd and his co-workers. The uridine compound was obtained by condensing a protected uridine-5′-benzyl phosphorochloridate with tetramethylammonium tribenzyl pyrophosphate to form the protected uridine-5′-tetrabenzyl triphosphate, which on debenzylation by hot phenol and then hydrogenolysis to remove the benzyl groups, followed by hydrolysis, gave the triphosphate (isolated as the sodium salt):



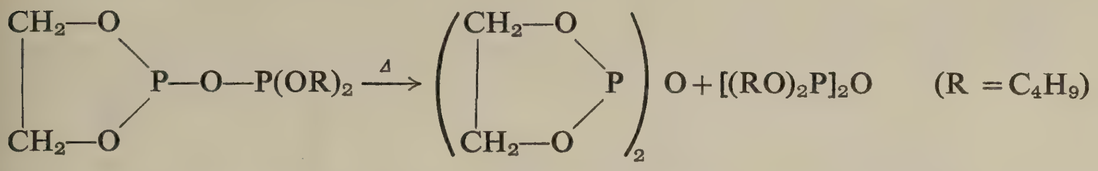
## ESTERS OF PYROPHOSPHOROUS ACID, $(RO)_2P–O–P(OR)_2$

The action of bromine[1584,1616] or chlorine[1617] or 1,2-dibromoethane,[1714] on sodium dialkyl phosphites gives a complex mixture of products. For example, sodium diethyl phosphite and bromine form a mixture of diethyl phosphite, triethyl phosphate, tetraethyl pyrophosphite, tetraethyl pyrophosphate and tetraethyl hypophosphite.[1584] Tetraesters of pyrophosphorous acid have generally been made by the reaction between a salt of a dialkyl phosphite and a dialkyl phosphorochloridite,[1602,1614,1616,1618,1621] or by the controlled action of water on dialkyl phosphorochloridite, usually in the presence of a tertiary organic base[1615,1619]:

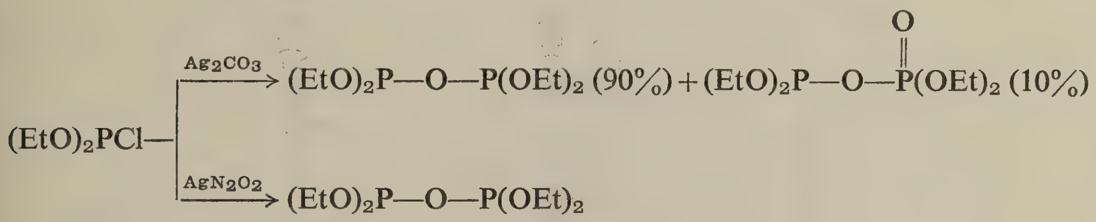
$$(R'O)_2PONa + (RO)_2PCl \rightarrow (R'O)_2P—O—P(OR)_2$$
$$2(RO)_2PCl \xrightarrow[-2R_3N,HCl]{H_2O+2R_3N} (RO)_2P—O—P(OR)_2$$

In addition to simple tetra-alkyl pyrophosphites a number of derivatives are known in which the phosphorus atom forms part of a 1,3-dioxa-2-phospha-ring system.

[1614–5,1618–9] Yields of the higher unsymmetrical esters are reduced by symmetrization during distillation[1615,1619]:



Tetraethyl pyrophosphite has been prepared, together with some 10% tetraethyl isohypophosphate, by the action of silver carbonate on diethyl phosphorochloridite,[1543] or by reaction of the chloridite with silver hyponitrite[638]:



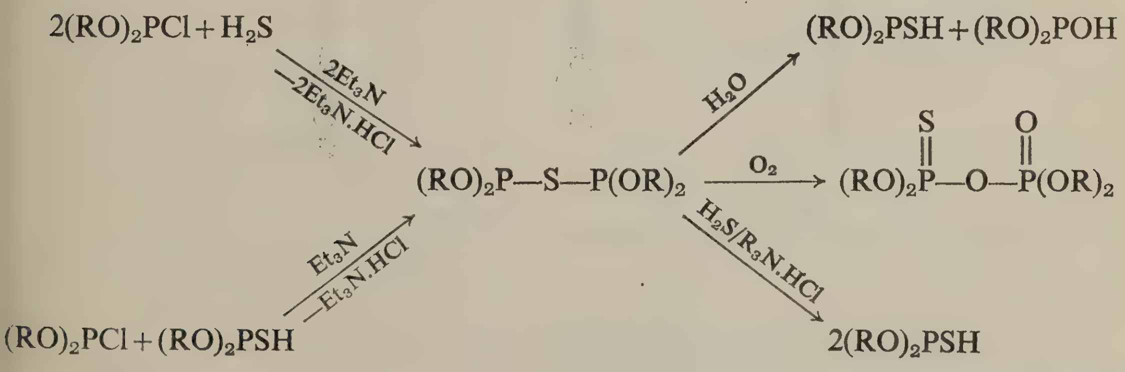
The lower tetra-alkyl pyrophosphites are liquids which can be distilled under vacuum without decomposition. In many of their properties they resemble tertiary phosphites. They react with 2 moles of iodine[1584,1616] and form adducts with 2 moles of cuprous halide.[1584,1614–5] They are readily oxidized, particularly by dinitrogen tetroxide,[862] to form tetraesters of pyrophosphoric acid; addition of sulphur[1602,1614–5] or selenium[1602] gives dithio- or diseleno-pyrophosphate, respectively. Hydrolysis is exothermic, giving 2 moles of dialkyl phosphite.[1584,1615] Carboxylic acids and amines readily cause P–O–P group fission to form acyl phosphite[1613,1621] and *N*-substituted dialkyl phosphoramidite[1621,1624] respectively.

Amides, particularly peptides, are conveniently prepared under mild conditions by adding tetraethyl pyrophosphite to a mixture of amine and acid in diethyl phosphite solvent[1621–2]; higher yields are claimed for bis-*o*-phenylene pyrophosphite,[1620] a reagent which is prepared by the action of water vapour *in vacuo* on *o*-phenylene phosphorochloridite[1619]:

$$(RO)_2P{-}O{-}P(OR)_2 + R'CO_2H \rightarrow (RO)_2POCOR' + (RO)_2POH$$
$$(RO)_2POCOR' + R''NH_2 \rightarrow R'CONHR'' + (RO)_2POH$$

Some reactions of pyrophosphites are shown in Chart XIX.

Tetra-alkyl thiopyrophosphites are prepared by the action of hydrogen sulphide on dialkyl phosphorochloridites in the presence of a strong organic base such as triethylamine, or from the chloridite and a dialkyl thiophosphite.[634] The compounds are highly susceptible to atmospheric oxidation, yielding tetra-alkyl monothionopyrophosphate. They are readily hydrolyzed and react with hydrogen sulphide in the presence of an amine hydrochloride giving dialkyl thiophosphite[634]:



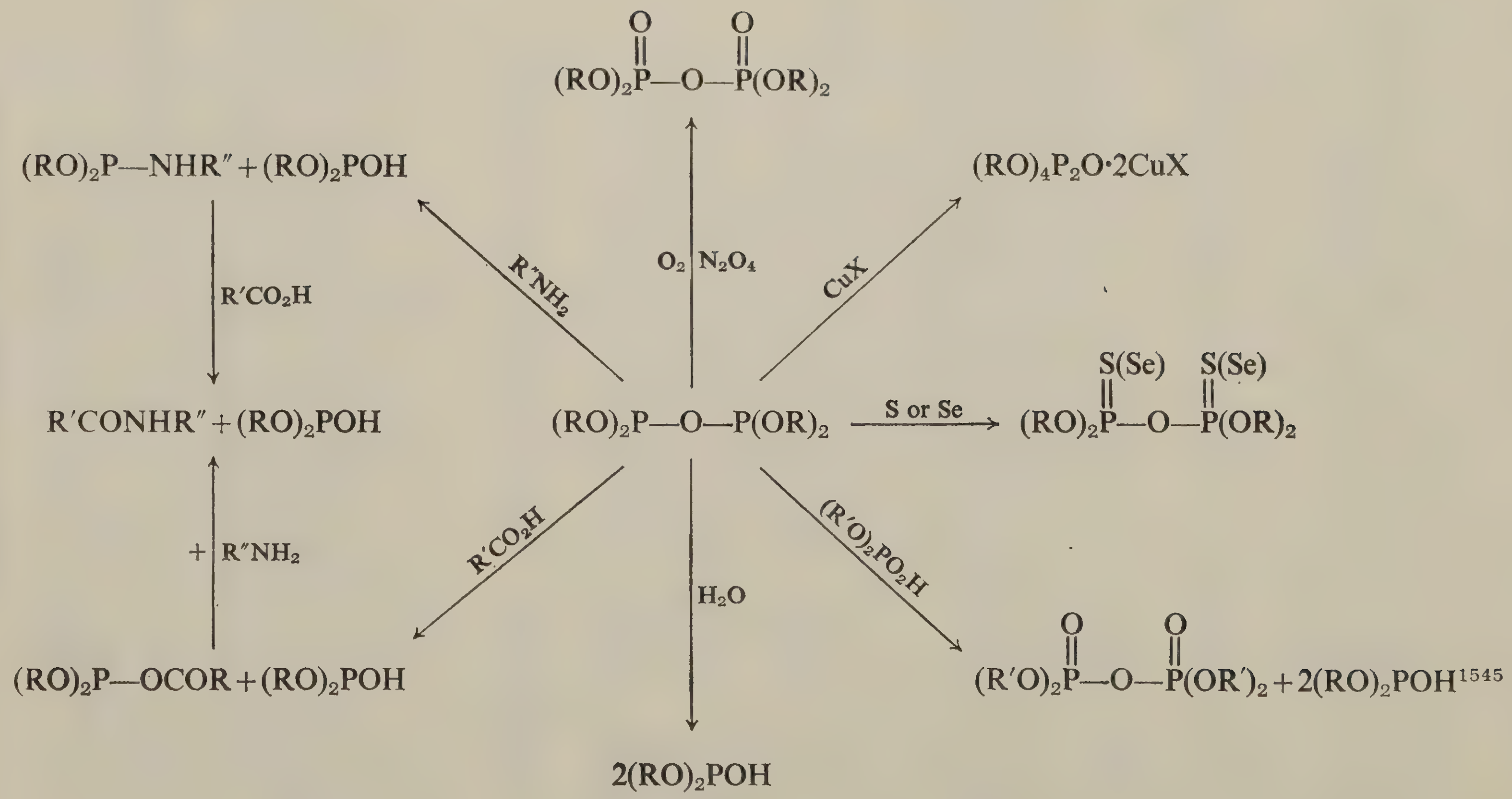
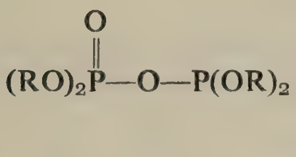


CHART XIX.—Some reactions of pyrophosphites

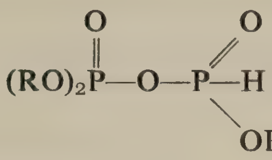
## Esters of Phosphorous Phosphoric Anhydride (isoHypophosphates)

Tetra-alkyl isohypophosphates $R_4P_2O_6$ (I) which are isomeric with tetra-alkyl hypophosphate (III) and with trialkyl esters of alkyl phosphonic-phosphoric anhydride (IV) may be readily obtained by reaction of a phosphorochloridite with a dialkyl phosphate[1638]:

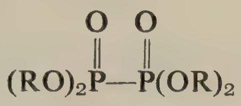


$(RO)_2\overset{O}{\overset{\|}{P}}-O-P(OR)_2$

I

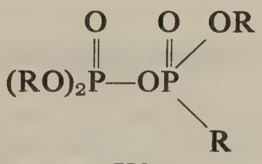


II

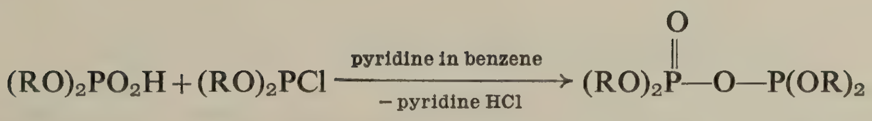


$(RO)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{P}}(OR)_2$

III

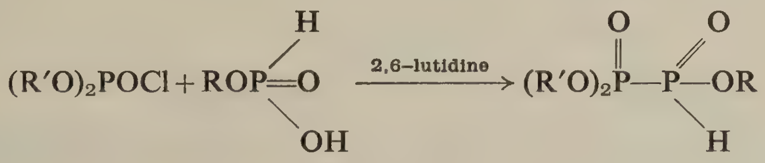


IV

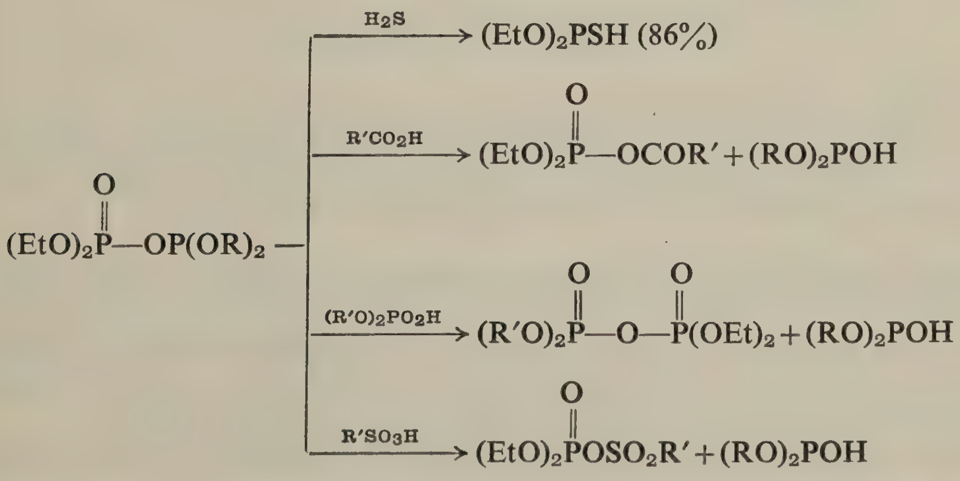


$$(RO)_2PO_2H + (RO)_2PCl \xrightarrow[-\text{ pyridine HCl}]{\text{pyridine in benzene}} (RO)_2\overset{O}{\overset{\|}{P}}-O-P(OR)_2$$

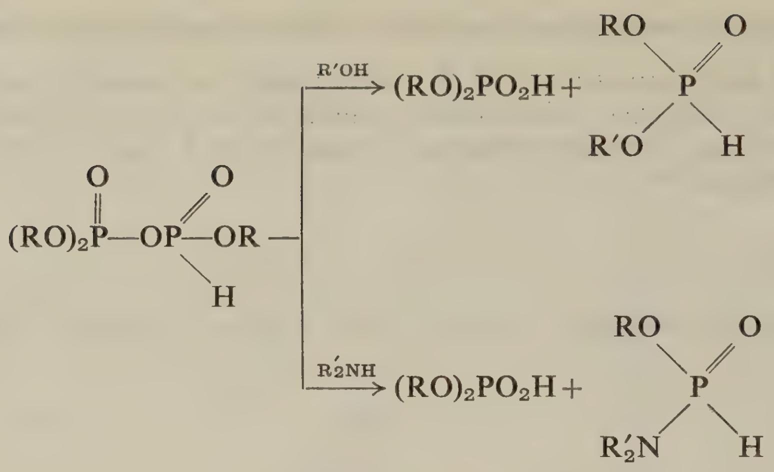
Trialkyl isohypophosphates (II) are formed from dialkyl phosphorochloridate and monoalkyl phosphite:



The tetra-alkyl esters react with hydrogen sulphide, giving dialkyl phosphorothioite,[1640] and with acids to form mixed anhydrides of phosphoric acid.[1639] The triesters have been used by Todd and co-workers to prepare complex unsymmetrical dialkyl phosphites as intermediates for nucleotide synthesis.[1598] They react with amines giving *O*,*N*,*N*-trialkyl phosphoramidites.[1641]



**Refs. p. 1082**



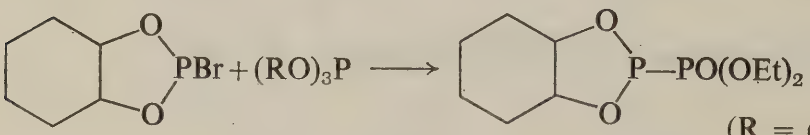
## Esters of Hypodiphosphorous Acid

Tetra-alkyl or aryl esters of hypodiphosphorous acid are claimed to be prepared by the reduction of phosphorochloridites with metallic sodium. Similar reactions with phosphorodichloridites are said to form compounds of the type RO—P=P—OR[1633]:

$$(RX)_2PCl \xrightarrow{Na} (RX)_2P\text{—}P(XR)_2 \qquad (X = O, S)$$

The reaction of diphosphorus tetraiodide with phenol gives a reasonable yield of tetraphenyl hypodiphosphite, but Grignard reagents, alcohols and amines cause fission of the P–P bond.[1635]

Low yields of hypodiphosphorous phosphoric esters are obtained by the reaction of catechol phosphorobromidite with trialkyl phosphites[877]:



(R = ethyl and higher alkyls)

## Esters of Hypophosphorous Acid

Methyl and ethyl hypophosphites were first prepared in 1960 by Kabachnik and co-workers[1636] by alkylating hypophosphorous acid with the appropriate diazoalkane: only one equivalent of diazoalkane reacts, regardless of the amount used:

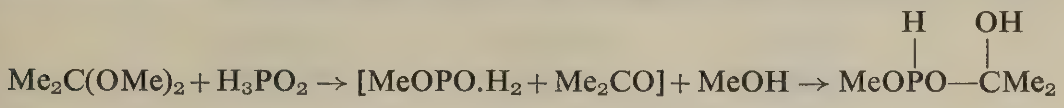
$$CH_2N_2 + H_3PO_2 \xrightarrow{\text{ether}} MeOPO.H_2 + N_2$$

The distilled esters decompose rapidly at room temperature but can be stored at $-60°C$. More recently it has been shown that compounds having an ortho-carbonyl function, such as orthocarbonates, orthocarboxylates, ketals and acetals, react with anhydrous hypophosphorous acid giving alkyl hypophosphites[1637]:

$$H_3PO_2 + R_nC(OR')_{4-n} \rightarrow ROPO.H_2 + R'OH + RCO(OR)_{2-n} \qquad (n = 0, 1, 2)$$

Methyl and ethyl hypophosphites, obtained by mixing methyl or ethyl orthoformate with hypophosphorous acid at room temperature followed by vacuum distillation, have been characterized by nuclear magnetic resonance spectroscopy.

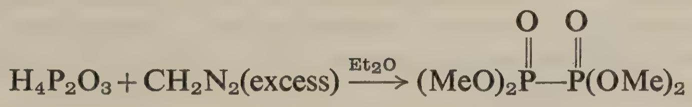
Acetone dimethyl ketal and hypophosphorous acid react giving methyl(1-hydroxy-1, 1-dimethyl)methyl phosphinate, which is believed to result from addition of by-product acetone to the initially formed methyl hypophosphite:



$$Me_2C(OMe)_2 + H_3PO_2 \rightarrow [MeOPO.H_2 + Me_2CO] + MeOH \rightarrow MeO\overset{H}{\overset{|}{P}}O\text{—}\overset{OH}{\overset{|}{C}}Me_2$$

## Esters of Hypophosphoric Acid

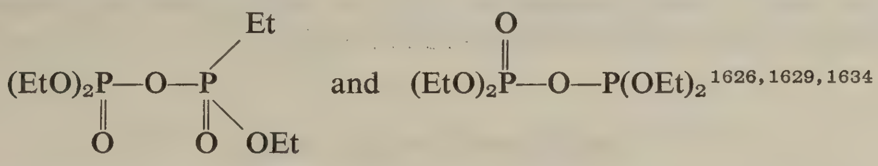
Tetramethyl and tetraethyl esters of hypophosphoric acid are best prepared by the action of an ethereal solution of diazomethane or diazoethane on the anhydrous acid[1625-6]:



$$H_4P_2O_3 + CH_2N_2(\text{excess}) \xrightarrow{Et_2O} (MeO)_2\overset{O}{\overset{\|}{P}}\text{—}\overset{O}{\overset{\|}{P}}(OMe)_2$$

The presence of the P–P bond in the compounds is shown by lack of reactivity with cuprous halides, iodine and other mild oxidizing agents. The Raman spectrum shows a strong band at 260 cm.$^{-1}$ in the methyl compound. This is comparable with that at 274 cm.$^{-1}$ in the acid and is assigned to the P–P skeletal vibration.[1625-6] The action of methyl iodide on tetrasilver hypophosphate gives a mixture of tetramethyl hypophosphate and tetramethyl pyrophosphate.[1628]

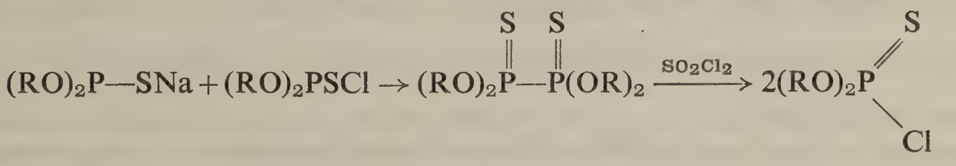
Attempts to build hypophosphate esters from two monophosphorus-containing components have so far been only partially successful, owing to concurrent formation of esters having P–O–P bonds. Diethyl phosphorochloridate is reduced by sodium in toluene to form some 65% tetraethyl hypophosphate together with tetraethyl pyrophosphate.[1626-7] Condensation of the chloridite with sodium diethyl phosphite gives up to a 53% yield[1629] but thermal condensation with triethyl phosphite gives largely a mixture of:



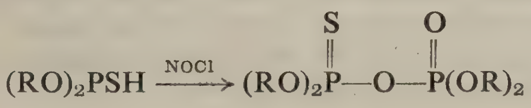
Hypophosphates are also formed by the action of sulphuryl chloride on sodium dialkyl phosphites[1629, 1714] (whereas the action of bromine gives a mixture of products[1584, 1714]) and by thermal decomposition of bis-dialkoxyphosphinyl mercury compounds.[686]

Tetraethyl hypophosphate can be hydrolyzed almost quantitatively to diethyl phosphite and diethyl phosphate[1626, 1630]; chlorination with sulphuryl chloride gives 2 moles of diethyl phosphorochloridate.[1630]

Tetra-alkyl dithiohypophosphates have been prepared in good yield by the condensation of a sodium dialkyl thiophosphite with a dialkyl phosphorochloridothionate.[1632] They react with sulphuryl chloride in carbon tetrachloride to form 2 moles of dialkyl phosphorochloridothionate:



An earlier reported preparation of these compounds by the action of nitrosyl chloride on dialkyl thiophosphite[1631] is stated to yield a tetra-alkyl monothiopyrophosphate and not a dithiohypophosphate[1632]:



$$(RO)_2PSH \xrightarrow{NOCl} (RO)_2\overset{S}{\overset{\|}{P}}\text{—}O\text{—}\overset{O}{\overset{\|}{P}}(OR)_2$$

## AMINO PHOSPHINES

The 'amino phosphines' comprise derivatives of the following:

| $P(NH_2)_3$ | $RP(NH_2)_2$ | $R_2P(NH_2)$ |
|---|---|---|
| phosphorous triamide | phosphonous diamide | phosphinous amide |

### Derivatives of Ammonia

The halogen atom attached to phosphorus in phosphorus trihalides, phosphonous dihalides and phosphinous halides is readily replaced on ammonolysis. However, the primary products of these reactions, phosphorous triamide, phosphonous diamide and phosphinous amide, have been isolated in only a few special cases, owing to such factors as instability of the compounds and the difficulty of separation from by-product ammonium halide.

Attempts to make aminodimethylphosphine by ammonolysis of dimethyl chlorophosphine or *N*,*N*-dimethyl dimethylphosphinous amide give only a mixture of the poly(dimethylphosphino) amines, $(Me_2P)_2NH$ and $(Me_2P)_3N$.[334] In contrast the aminophosphine $(CF_3)_2PNH_2$, a colourless liquid, is thermally stable up to 250°C. *in vacuo* and shows no direct conversion into poly(bis-trifluoromethyl phosphinyl) amines[249] which are prepared by the reactions indicated below[2147]:

$$(CF_3)_2PNH_2 + (CF_3)_2PCl \xrightarrow{Me_3N} [(CF_3)_2P]_2NH \qquad \text{(decomposes slowly at 300°C.)}$$

$$[(CF_3)_2P]_2NH \xrightarrow{Na/NH_3} [(CF_3)_2P]_2N^-Na^+ \xrightarrow{(CF_3)_2PCl} [(CF_3)_2P]_3N \qquad \text{(decomposes at 150°C.)}$$

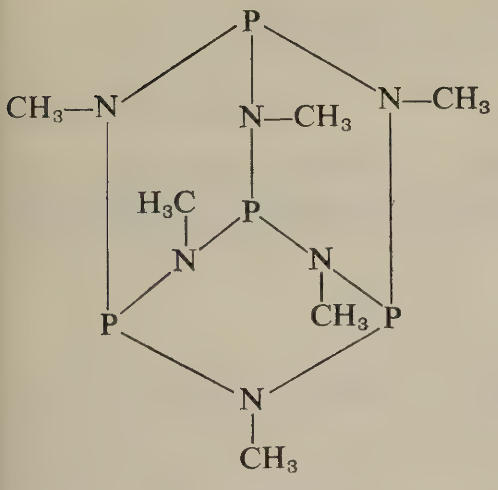
A few ester derivatives of phosphoramidous acid $[(HO)_2PNH_2]$ and phosphorodiamidous acid $[HOP(NH_2)_2]$ are reported; diphenyl phosphoramidite, $(PhO)_2PNH_2$, decomposes even at room temperature giving off white phosphorus; phenyl phosphorodiamidite is reported to be an amorphous solid, m.p. 110°–112° (decomp.).[386]

### Derivatives of Primary Amines

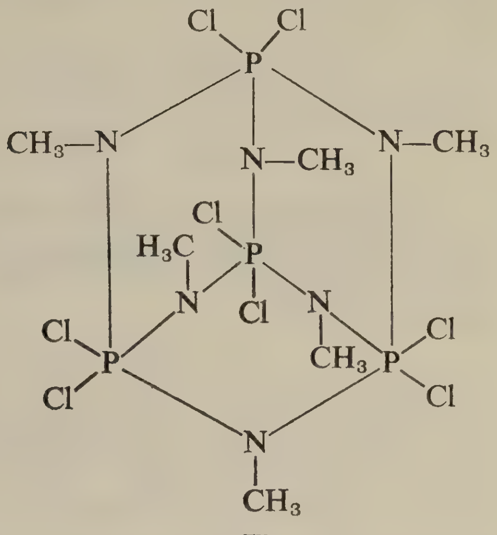
Michaelis[943] showed that the initial reaction of a primary amine with phosphorus trichloride affords an *N*-alkyl phosphoramidous dichloride, $RNHPCl_2$. The lower alkyl members of this class of compounds may be distilled *in vacuo* without decomposition. But, in general, compounds of this type, characterized by a group –NH–PX–, are unstable to heat and readily undergo condensation and transformation to other substances. The nature of the products becomes increasingly ill-defined with further replacement of chlorine on the phosphorus atom by primary amine. Until recently the literature showed no successful characterization of a P–N compound derived from phosphorus trichloride and a primary amine. By working with an excess of methylamine over phosphorus trichloride, and in the absence of a solvent, Holmes and Forstner isolated a compound $P_4N_6(CH_3)_6$, **I**, a member of a new class of P–N compounds, having a cage-like structure analogous to tetraphosphorus hexa-oxide in which the oxygen atoms are replaced by $>$N–Me groups.[711] A related compound $P_4N_6(CH_3)_6Cl_8$, **II**, having two chlorine atoms attached to each phosphorus atom, has been made by interaction of phosphorus pentachloride and methylamine hydrochloride.[1540]

Aryl phosphonous and phosphinous halides react with primary *tert*-alkyl aliphatic amines and aromatic amines to give well-defined products having sharp melting-points. Typical of such products are *N*-substituted diphenyl phosphinamidites, $Ph_2PNHR$[2151] and *N*,*N'*-di*tert*-butyl phenyl phosphonous diamide,[539] and bis-(diphenylphosphino) methylamine.[588] With aryl hydrazines, phosphonous halides give compounds of the type PhP═NNHAr.[388]

Aromatic amines react with phosphorus trichloride to give not *N*-aryl phosphoramidous dichloride but a compound named by Michaelis[2168] as a phosphazochloride



I



II

as the initial product. Phenyl phosphazochloride was shown by Michaelis to be dimeric in solution. It is best prepared by the reaction of phosphorus trichloride and aniline hydrochloride:

$$2PhNH_3^+Cl^- + 2PCl_3 \rightarrow (PhN{=}PCl)_2 + 2HCl\uparrow$$

Further reaction of these compounds with aromatic amines,[2168] or the reaction of phosphorus trichloride with five equivalents of aromatic amine, yields compounds of the phosphorazo class RN=PNHR:

$$5PhNH_2 + PCl_3 \rightarrow (PhN{=}P{-}NHPh) + 3PhNH_3Cl$$

A few compounds of this class have been characterized by Grimmel[1580] and exhibit dimeric behaviour in solution, as well as one compound, *p*-methoxyphenyl-*N*-bis(*p*-methoxyiminophosphine), which is monomeric in benzene solution.[2164] Phosphazo-compounds are of interest for the preparation of amides, particularly peptides. When phosphorus trichloride is added to a mixture of an amine and a carboxylic acid in an inert solvent the phosphazo-compound is formed and reacts with the carboxylic acid, giving the amide[1580, 2165-6]:

$$R{-}N{=}P{-}NHR + 2R'CO_2H \rightarrow 2R'CONHR + HPO_3$$

Related reactions are those which employ 'phosphite amides' *O,O*-dialkyl *N*-substituted phosphoramidites, formed *in situ* by reaction of amino compounds and dialkyl phosphorochloridites, for the synthesis of peptides.[2167]

### Derivatives of Secondary Amines

Secondary amines and phosphorus trichloride react exothermically to produce by successive substitution *N,N*-disubstituted phosphoramidous dichlorides, bis-(*N,N*-disubstituted) phosphorodiamidous chlorides and tris-(*N,N*-disubstituted) phosphorous triamides[943]:

$$PCl_3 \xrightarrow[-\ NH,HCl]{+2R_2NH} R_2NPCl_2 \rightarrow (R_2N)_2PCl \rightarrow (R_2N)_3P$$

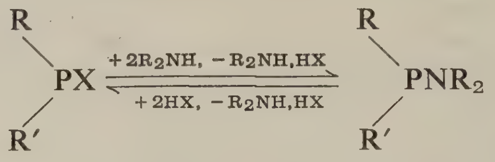
**Refs. p. 1082**

In like manner, phosphonous dichlorides form the *N*,*N*-disubstituted phosphonamidous chloride and then bis-(*N*,*N*-disubstituted) phosphonous diamide. Phosphinous halides form *N*,*N*-disubstituted phosphinous amide[384,388,446,539,588,703,943,2094,2431]:

$$R'PCl_2 \xrightarrow[-R_2NH,HCl]{+2R_2NH} R'P(NR_2)Cl \rightarrow R'P(NR_2)_2$$

$$R'_2PCl \xrightarrow[-R_2NH,HCl]{+2R_2NH} R'_2PNR_2$$

Aminohalogenophosphines, $R'P(NR_2)X$ (where $X = Cl$, Br, I; $R' = R_2N$, alkyl, aryl or halogen), can be prepared by treating aminophosphines with anhydrous hydrogen halide,[68,334,336,477,767] and by aminolysis of the corresponding halophosphine[384,2151]:



by coproportionation of halogenophosphine and aminophosphine,[647,756]

$$(R_3N)_3P + 2PCl_3 \rightarrow 3PCl_2NR_2$$

and by the action of Grignard reagents (or, better, organolithium compounds) on $R_2NPX.R$.[68,334,336,767] The chlorine atoms of *N*,*N*-dimethyl phosphoramidous dichloride are readily replaced by cyano-groups through the agency of silver cyanide[767]:

$$Me_2NPCl_2 \xrightarrow{AgCN} Me_2NP(CN)_2$$

Ligand exchange between the following pairs of compounds, $PCl_3:P(NEt_2)_3$, $PCl_3:ClP(NEt_2)_2$, $MePCl_2:MeP(NMe_2)_2$, $MePCl_2:MeP(NEt_2)_2$, $MePBr_2:MeP(NMe_2)_2$ and $MePBr_2:MeP(NEt_2)_2$ was investigated by Van Wazer and Maier.[756] In all cases the equilibrium constant for disproportionation of the intermediate products, obtained by exchanging halogen for dialkyl amino-groups, was found to be so small that it could not be determined within experimental error from the stoicheiometry of the products.

In contrast with phosphonous chlorides and phosphinous chlorides, which undergo both oxidation and fluorination with arsenic or antimony trifluoride giving derivatives of phosphorus pentafluoride,[556,891,991] *N*,*N*-dialkyl phosphoramidous chlorides and alkyl phosphorodichloridites undergo normal exchange to form *N*,*N*-dialkyl phosphoramidous difluorides and alkyl phosphorofluoridites, respectively[981]:

$$YPCl_2 \xrightarrow{SbF_3} YPF_2 \qquad (Y = R_2N\text{—}, RO\text{—})$$

The dialkylaminofluorophosphines are interesting ligands; they will displace carbon monoxide from nickel and molybdenum carbonyls, giving compounds of the type $Ni(CO)_2L_2$, $NiL_4$ and $Mo(CO)_3L_3$ (where $L = Me_2NPF_2$, $Et_2NPF_2$).

Alkyl/aryl dialkylaminochlorophosphines react like the halogenophosphines with $As/SbF_3$ giving alkyl/aryl dialkylaminofluorophosphoranes[2431]:

$$3RPCl.NR'_2 + 3MF_3 \rightarrow 3RPF_3NR'_2 + 2M + MCl_3 \qquad (M = As, Sb)$$

They may be converted to the corresponding fluorophosphines by reaction with sodium fluoride in tetramethylene sulphone[2431]:

$$RPCl.NR'_2 + NaF \rightarrow RPF.NR'_2 \qquad (R = Me, Ph, R'_2N)$$

Diethylamino tri- and tetra-fluorophosphoranes are obtained from $PF_5$ or $PhPF_4$ respectively by reaction with diethylaminotrimethyl silane[2142]:

$$RPF_4 + Me_3SiNEt_2 \rightarrow RP(NEt_2)F_3 + Me_3SiF \qquad (R = Ph, Et_2N)$$

Aminolysis of difluorotrifluoromethyl phosphine with dimethylamine proceeds abnormally to give a mixture of the expected product, *N,N*-dimethyl trifluoromethyl phosphonamidous fluoride, and dimethylammonium hydrotetrafluorotrifluoromethyl phosphate:

$$3CF_3PF_2 + 3Me_2NH \rightarrow 2CF_3PF(NMe_2) + Me_2NH_2^+ + CF_3PF_4H^-$$

The structure of the anion was confirmed by infra-red and n.m.r. spectroscopy.[455]

## Reactions of Dialkylaminophosphines

The aminophosphines form a class of highly reactive compounds. Many of their reactions resemble those of tertiary phosphines. They are readily oxidized by atmospheric oxygen and react exothermically with sulphur at room temperature. Such reactions are best conducted at a controlled temperature in an inert solvent if product isolation is desired[2]:

$$A_2PNR_2 \rightarrow A_2PX.NR_2 \qquad (X = O, S; A = \text{alkyl, aryl}, R_2N)$$

The compounds readily undergo a quaternization reaction with compounds such as alkyl halides, *N*-halogenoamines, sulphenyl chlorides and halogens to form quasiphosphonium salts (see page 941):

$$A_2PNR_2 + R'X \rightarrow A_2\overset{+}{P}(NR_2)R'X^- \qquad (R' = \text{alkyl, RS—}, R_2N, \text{halogen})$$

Aminophosphines are good ligands. Complexes with mercury(II), cadmium(II), copper(I), nickel(II) and cobalt(II) are reported.[384, 633] Cadmium and mercury iodides form complexes of the type $A_2PNR_2,MI_2$ and $[A_2PNR_2]_2,MI_2$ (where $M = Cd$, $Hg$; $R =$ lower alkyl; $A = R_2N$, $R_2'N$, phenyl). The cuprous iodide complex of *N,N*-diethyl diphenyl phosphinamidite is a tetramer in benzene solution, $[Ph_2PNEt_2,CuI]_4$, in keeping with the behaviour of cuprous iodide complexes of simple phosphines.[384] Hexa-*N*-methyl phosphorous triamide will displace one or two carbon monoxide ligands from nickel carbonyl to form complexes $(Me_2N)_3P,Ni(CO)_3$ and $[(Me_2N)_3P]_2,Ni(CO)_2$. Tetra-*N*-methyl phosphorodiamidous chloride and tetra-*N*-methyl cyanophosphorous diamide form the complexes $[(Me_2N)_2PX]_2,Ni(CO)_2$ (where $X = Cl$ or $CN$).[633]

The borine complex $(Me_2N)_3P,BH_3$ is particularly stable; it decomposes only above 250°C. In contrast, the borine complex of bis-(dimethylamino)phosphine, $(Me_2N)_2PH,BH_3$, made by reduction of bis-(dimethylamino)chlorophosphine with lithium borohydride, decomposes slowly at room temperature; the borine complex of dimethylaminophosphine, $Me_2NPH_2,BH_2$, could not be made by a similar method.[860]

The P–N bond in phosphorous amides is readily broken by acid hydrolysis and by protic reagents such as alcohols, mercaptans, anhydrous halogen acids and by other amines, with elimination of amine and formation of a phosphorous *O*-ester, *S*-ester, halide or another amino-compound, respectively:

$$A_2PNMe_2 + BXH \rightarrow A_2PXB + Me_2NH$$
$$(X = O, S; A = \text{alkoxy, dialkylamino})^{388, 2149}$$
$$A_2PNMe_2 + PhNH_2 \rightarrow A_2PNHPh + Me_2NH^{2170}$$

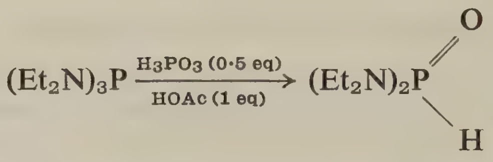
In compounds having more than one P–N bond, use of an excess of protic reagent leads to the complete elimination of the nitrogen component from the phosphorus atom. By careful control of reagent quantities intermediate amino-esters can be obtained:

$$(Me_2N)_3P + EtOH \rightarrow (Me_2N)_2POEt \text{ (82\% yield)} + Me_2NH^{2149}$$
$$(Me_2N)_3P + 3EtOH \rightarrow (EtO)_3P \text{ (91·2\% yield)} + 3Me_2NH^{2170}$$

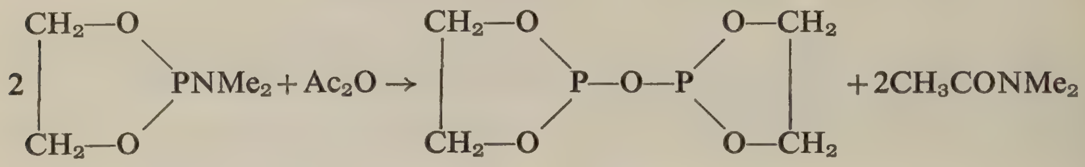
Carboxylic acids react to form carboxylic acid amide and a phosphorous acid derivative, e.g.,

$$(Me_2N)_3P + 3CH_3CO_2H \rightarrow 3CH_3CONMe_2 + H_3PO_3{}^{2170}$$

Bis-*N*,*N*-diethylaminophosphine oxide can be made from tris-(diethylamino) phosphine by treatment with one equivalent of acetic acid[2149] or with phosphorous acid[2169]:



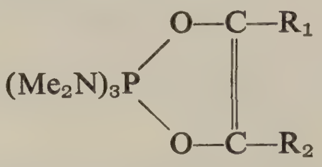
Diethylene pyrophosphite is formed by the action of acetic anhydride on *N*,*N*-dimethyl ethylene phosphoramidite[2149]; acetyl ethylene phosphite is a possible intermediate:



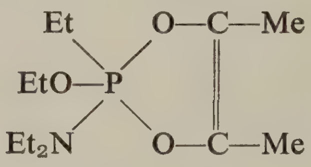
Like the amides of other Groups IV and V elements, phosphorous amides combine readily with compounds having multiple unsaturation such as carbon dioxide and disulphide, organic isocyanates and organic isothiocyanates to form phosphorylated carbamates and ureas[698, 2170]:

$$R_nP(NMe_2)_{3-n} + (3-n)CS_2 \rightarrow R_nP(SCS.NMe_2)_{3-n}$$
$$R_nP(NMe_2)_{3-n} + (3-n)PhNCS \rightarrow R_nP(PhNCS.NMe_2)_{3-n}$$
$$(R = \text{alkyl, aryl}; n = 0, 1, 2)$$

Phosphorous triamides are reported to react like trialkyl phosphites with $\alpha$-$\beta$ dicarbonyl compounds to form phosphorane derivatives. Tris-(dimethylamino) phosphine and benzil or diethyl mesoxalate react exothermically to form the compound **I** in high yield[96]; *N*,*N*,*O*-triethyl ethyl phosphonamidite and diacetyl form the related compound **II**.[2141]

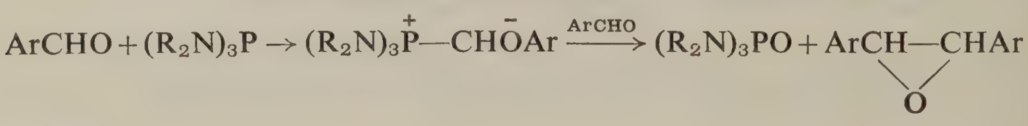


($R_1$ = OEt, $R_2$ = $CO_2Et$
or $R_1$ = $R_2$ = phenyl)
**I**



**II**

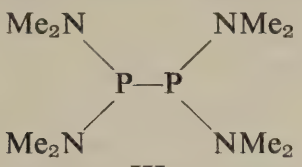
Molar quantities of aromatic aldehydes and tris-(dialkylamino)phosphines react to form solid salt-like quasiphosphonium betaines which interact with more aldehyde to form a mixture of *cis*- and *trans*-stilbene and tris-(dialkylamino)phosphine oxide[739]:



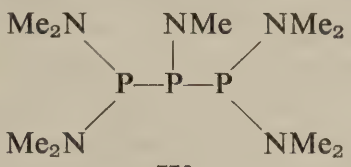
$$ArCHO + (R_2N)_3P \rightarrow (R_2N)_3\overset{+}{P}—CH\overset{-}{O}Ar \xrightarrow{ArCHO} (R_2N)_3PO + ArCH—CHAr$$

### Amino-derivatives of Di- and Poly-phosphines

Reduction of bis(dimethylamino)chlorophosphine with sodium in hexane solution affords rather poor yields of tetrakis-(dimethylamino)diphosphine **III** and pentakis-(dimethylamino)triphosphine, m.p. 18°–20°C., **IV**, together with products of side reactions which correspond to the disproportionation of the starting material.[647]



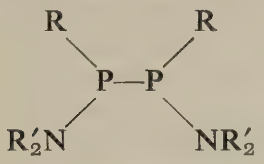
**III**



**IV**

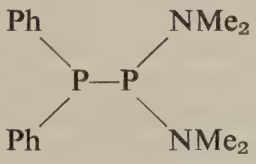
The diphosphine derivative is a solid, m.p. 48°. It forms adducts with oxygen, sulphur and diborane in which the P–P bond remains intact, but with hydrogen chloride, methyl iodide, phosphorus trichloride and on heating, partial P–P bond fission occurs giving a mixture of products.

Symmetrical and unsymmetrical di-substituted bis(dialkylamino)diphosphines **V** and **VI** have been described.

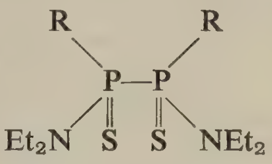


R = phenyl, *cyclo*hexyl, ethyl

**V**



**VI**



R = *cyclo*hexyl

**VII**

The symmetrical compounds may be obtained in reasonably good yield by reduction of *N*,*N*-dialkyl alkyl (or phenyl) phosphonamidous chloride with sodium–potassium alloy in ether[703] or from *sym*-diphenyl diiododiphosphine and dimethylamine.[733] Compound **VI** was obtained by condensing sodium diphenyl phosphine with bis-(dimethylamino)chlorophosphine.[733] Compound **V** (R = *cyclo*hexyl) reacts with sulphur giving two crystalline products suggested to be the racemic and meso forms of *P*,*P′*-di*cyclo*hexyl-*P*,*P′*-diethylamino-diphosphine disulphide **VII**.[703] Compound **VI** forms a diborine adduct; it also decomposes readily on heating to tetraphenyl diphosphine and $(C_6H_5)_2P.PNMe_2.P(C_6H_5)_2$.[733]

## IMINO DERIVATIVES OF ORGANOPHOSPHORUS COMPOUNDS

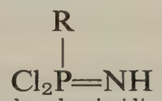
Compounds described in this section are pentavalent compounds of phosphorus which contain a real or potential phosphorus–nitrogen double bond. Parent structures and nomenclature of such compounds are indicated below. One book[2278] and several reviews[2195] are concerned with compounds in these classes.

$R_3P{=}NR'$
phosphine imide

$Cl_3P{=}NH$
phosphorimidic trichloride

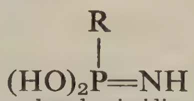
$(HO)_3P{=}NH$
phosphorimidic acid

$R_3P{=}N{-}N{=}CR_2$
phosphazines



$Cl_2\overset{R}{\overset{|}{P}}{=}NH$

phosphonimidic dichloride

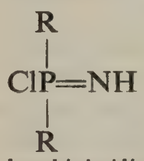


$(HO)_2\overset{R}{\overset{|}{P}}{=}NH$

phosphonimidic acid

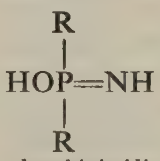
$R_3P{=}N{-}N{=}N{-}R$

phosphazides



$Cl\overset{R}{\overset{|}{\underset{R}{\underset{|}{P}}}}{=}NH$

phosphinimidic chloride



$HO\overset{R}{\overset{|}{\underset{R}{\underset{|}{P}}}}{=}NH$

phosphinimidic acid

### Phosphine Imines (Iminophosphoranes, Phosphine Imides)

The preparation and properties of phosphine imines, $R_3P{=}NR'$ ($R$ = alkyl, aryl; $R'$ = alkyl, aryl, benzoyl), were first investigated by Staudinger and Hauser.[110] Although there are few reports of phosphine imines in which all the substituents on phosphorus are aliphatic,[110, 2185, 2225, 2263] numerous triaryl, generally triphenyl, phosphine imines are known and may be represented by the formula $R_3P{=}NY$ (where Y = alkyl,[2101, 2185] aryl,[2089, 2185, 2189] hydrogen,[2159] acyl,[2107, 2183, 2189] $RSO_2$–,[2183] $>SO_2$,[2246] $-PO(OR)_2$,[198] $-PO(R)_2$,[2273] $-CO_2R$,[2190] halogen (X),[2184] $-CONPh_2$,[2189] $-SiMe_3$,[2159, 2205] $-S^+Me_2X^-$, $-PPh_3{}^+X^-$,[2108] $PhC{=}CCl$–[2252] and amino.[2414] Compounds in which R = alkyl and Y is alkyl, phenyl or trimethylsilyl are liquids which can be purified by distillation under reduced pressure without decomposition.[110, 2159] When R is phenyl the compounds are frequently crystalline solids, which are often stable up to 150°C. and can be purified by sublimation or crystallization from inert solvents.

Relatively few unsubstituted phosphine imines have been made. The alkyl compounds, $R_3P{=}NH$ (R = ethyl, propyl, butyl),[2159] are colourless liquids which can be distilled under reduced pressure. Triphenylphosphine imine, m.p. 128°, is rapidly hydrolyzed to triphenylphosphine oxide in moist air but can be stored under a dry nitrogen atmosphere. It is soluble in inert organic media and is monomeric in benzene solution.[2106, 2182–3, 2205] Various other aryl compounds, $Ar_3P{=}NH$ (Ar = *o*-, *m*-, *p*-tolyl), and mixed ethyl phenylphosphine imines have been described.[2106] The aryl compounds are solids with well-defined melting points and are monomeric in solution. Reactions of triphenylphosphine imines are shown in Chart XX.

#### PROPERTIES

Phosphine imines may be regarded as members of the isoelectronic series $R_3PO$–$R_3PNH$ – $R_3PCH_2$, in which the nucleophilicity and basicity increase from left to right.[2260] They are the conjugate bases of *N*-quasiphosphonium salts, and the relationship is formally similar to that between phosphonium salts and methylene phosphoranes (see page 945):

$$R_3P=NR' \underset{-HX}{\overset{+HX}{\rightleftharpoons}} R_3P^+.NHR'X^-$$

They are basic in character and readily add hydrogen halides and react with alkyl halides to form *N*-quasiphosphonium salts.[11, 110, 2100, 2101, 2108] $pK_a$ values for two series of phosphine imines, *N*-(substituted phenyl) triphenylphosphine imines and *N*-phenyl tri-(*p*-substituted phenyl) phosphine imines in 95% ethanol solution are reported.[2293]

Staudinger noted that the properties of phosphine imines such as basicity, reactivity and stability to hydrolysis are determined to a large extent by the substituents attached to nitrogen and to phosphorus; for example, reactivity of compounds $R_3P{=}NPh$ decreases in the series R = alkyl > phenyl > benzyl.[110]

#### *Hydrolysis*

Phosphine imines undergo hydrolysis to tertiary phosphine oxides and amines:

$$R_3P{=}NR + H_2O \rightarrow [R_3P^+NHROH^-] \rightarrow R_3PO + RNH_2$$

The hydrolytic stability is greater when the phosphorus atom carries aromatic substituents and increases as the nitrogen atom carries more electropositive substituents, as in the series –*N*-alkyl < –*N*-aryl < –*N*-acyl < –*N*-$SO_2Ar$, or when the nitrogen carries a bulky substituent such as *tert*-butyl (cf. Table IX). The heats of hydrolysis of *N*-ethyl trimethylphosphine imine to $Me_3PO$ and of *N*-ethyl triphenylphosphine imine to $Ph_3PO$ in dilute hydrochloric acid have been determined, and bond dissociation energies $D(Me_3P{=}NEt) \simeq 97$ kcal./mole, $D(Ph_3P{=}NEt) \simeq 125$ kcal./mole have been calculated.[2185]

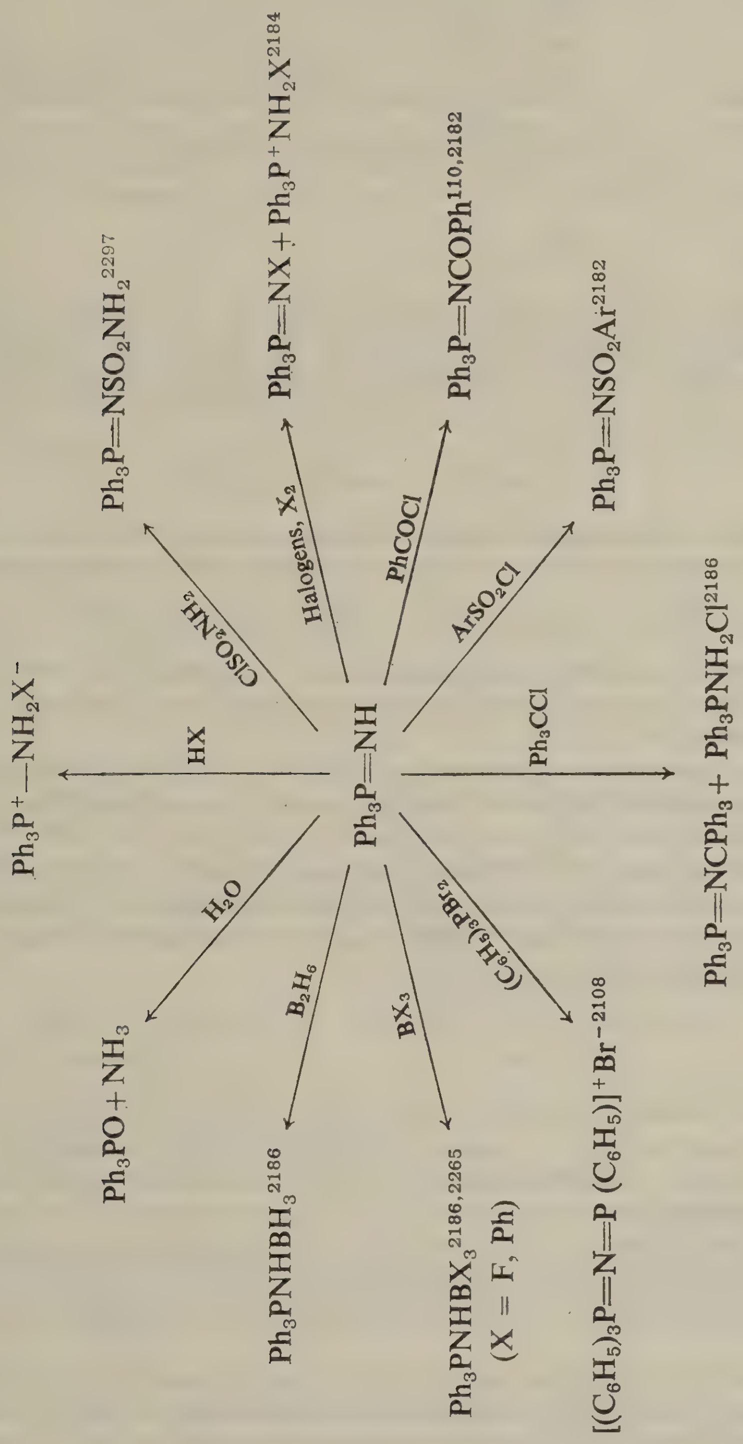


CHART XX.—Some reactions of triphenylphosphine imines

*Table IX.—Effect of Structure on Hydrolysis of Phosphine Imines*

| Phosphine imine | Conditions for hydrolysis | Ref. |
|---|---|---|
| $Et_3P{=}NEt$ | Hydrolyzed instantly with cold water | 2185 |
| $Ph_3P{=}NEt$ | Hydrolyzed by moist air | 2101 |
| $Ph_3P{=}N\text{-}t\text{-}Bu$ | Stable to moist air | 2101 |
| $Ph_3P{=}NAr$ | Dilute acid | 198 |
| $Ph_3P{=}NCO_2R$ | Boiling acid | 198 |
| $Ph_3P{=}NCOPh$ | Unaffected by boiling for 6 hr. with dilute acid | 2235 |
| $Ph_3P{=}NPOPh_2$ | Stable to boiling $H_2O$, dilute $H_2SO_4$, alcoholic NaOH | 2273 |
| $(Ph_3P{=}N)_2SO_2$ | Stable to boiling aqueous NaOH | 2246 |

### *Thermal Stability*

Phosphine imines having hydrogen atoms, alkyl or aryl groups attached to nitrogen are thermally stable and can frequently be purified by distillation under vacuum or by vacuum sublimation. Compounds with *N*-acyl substituents decompose at 150°–200°C. to form phosphine oxide and nitrile[110, 2235, 1987]:

$$RCON{=}PR_3 \xrightarrow{\Delta} RCN + R_3PO$$

Attempts to make *N*-thioacylphosphine imine by reaction of thioacyl azides and tertiary phosphines give a mixture of tertiary phosphine sulphide and nitrile[198]:

$$RCS.N_3 + R_3P \rightarrow [R_3P{=}NCS.R] \rightarrow R_3PS + RCN$$

*N*-Diphenylphosphinyl triphenylphosphine imines, e.g., $Ph_2PO.N{=}PPh_3$, are very stable thermally but the corresponding tributylphosphine imine decomposes at ambient temperature.[2273]

A number of workers have examined the ultra-violet and/or infra-red spectra of phosphine imines, and comparison of the spectra with those of phosphine oxides and methylene phosphoranes has aroused much interest.[198, 2100, 2246, 2257, 2264, 2284] Recently the infra-red spectra of *N*-phenyl triphenylphosphine imine, *N*-(toluene-*p*-sulphonyl) triphenylphosphine imine and *N*-(toluene-*p*-sulphonyl) phosphorimidic trichloride and the corresponding $^{15}N$-substituted compounds have been measured.[2257] The P=N absorption frequencies are:—

| $Ph_3P{=}NPh$ | $Ph_3P{=}NSO_2(p\text{-}CH_3{-}C_6H_4)$ | $Cl_3P{=}NSO_2(p{-}CH_3{-}C_6H_4)$ |
|---|---|---|
| 1344 cm.$^{-1}$ | 1147 cm.$^{-1}$ | 1199 cm.$^{-1}$ |

Like phosphine oxides, phosphine imines form adducts with many metal salts. The stability of these adducts is largely dependent on the *N*-substituent.[2260] Triphenylphosphine imine adducts with Co(II), Ni(II) and Cu(II) halides are reported.[2262] *N*-Phenyl triphenylphosphine imine forms highly stable solids, $Ph_3P{=}NPh.MI_2$ (M = Cd, Hg), when mixed with the metal iodide in benzene–acrylonitrile solvent, but complexes with transition metal salts such as $NiCl_2$, $CoCl_2$, e.g., $(Ph_3P{=}NPh)_2$, $MCl_2$, are unstable in solution and can be prepared only by fusing the components together.[2260]

Adducts of triphenylphosphine imine with boron compounds, $Ph_3P{=}NH,BX_3$ (X = H, F, Ph) are high-melting solids which are non-electrolytes in nitrobenzene solution.[2186] In the absence of water boron trifluoride and *N*-alkyl triphenylphosphine imines form complexes $Ph_3P{=}N^+R{-}BF_3^-$; if water is present the product is an alkylaminotriphenylphosphonium tetrafluoroborate. The stability of these complexes is very dependent on the nature of the alkyl group, R. When R = methyl or ethyl the complexes are stable to atmosphere, with R = *iso*propyl the complex decomposes slowly in air, and when R = *ter*-butyl the complex decomposes to its constituents under low vacuum.[2265]

The following metal alkyl–phosphine imine complexes are reported: $Ph_3P{=}NH,(CH_3)_3Al$ (dimeric in benzene),[2264] $R_3P{=}NSiMe_3,M(CH_3)_3$ (R = methyl, ethyl, phenyl; M = Al, Ga, In).[2263, 2298–300]

### PREPARATION OF PHOSPHINE IMINES

1. Reaction of tertiary phosphines with covalent azides (see p. 1072)
2. Reaction of *N*-chloro compounds with tertiary phosphines (see p. 1079)
3. From *N*-quasiphosphonium salts.

The elements of hydrogen halide are readily removed from amino- and mono-substituted amino-phosphonium salts by treatment with a suitable base such as liquid ammonia, triethylamine, sodamide or magnesium hydride[2101, 2105–6, 2108, 2182, 2261]:

$$R_3P^+NHR'X^- \xrightarrow{NaNH_2} R_3P{=}NR'$$

A convenient route to *N*-aryl triphenylphosphine imines is from dihalogenotriphenylphosphorane and an aromatic primary amine in the presence of triethylamine. The intermediate *N*-arylaminotriphenylphosphonium salts may be isolated when pyridine is used as base[177, 2100]:

$$Ph_3PBr_2 + ArNH_2 + 2Et_3N \rightarrow Ph_3P{=}NAr + 2Et_3N,HBr$$
$$Ph_3PBr_2 + ArNH_2 + C_5H_5N \rightarrow Ph_3P^+NHArBr^- + C_5H_5N,HBr$$

Similar reactions using aromatic diamines yield diphosphine imines. Amines such as 2,4,6-trichloro-, 2,4,6-tribromo- and 2,4,6-trimethyl-aniline do not react. Ammonia, primary aliphatic amines, hydrazine and phenyl hydrazine react with dibromotriphenylphosphorane, even in the presence of triethylamine, to form the phosphonium salt.[2100] Sodamide in liquid ammonia has been widely used to prepare strongly basic phosphine imines such as trialkyl- and triaryl-phosphine imines, alkyl arylphosphine imines and *N*-alkyl triphenylphosphine imines from the corresponding phosphonium salts.[2101, 2105–6, 2108, 2182]

A lithium chloride complex of dodecyl dimethylphosphine imine, $C_{12}H_{25}P(Me)_2{=}NH,LiCl$, is reported to be formed on reduction of dodecyl dimethylaminophosphonium chloride with butyl lithium; the free imine is obtained by distillation to break down the complex.[2255]

Triphenylphosphine imine has been obtained by the reaction[2106]:

$$[Ph_3P.NH_2]^+N_3^- + Ph_3P \xrightarrow[180-200°]{\Delta} 2Ph_3P{=}NH + N_2$$

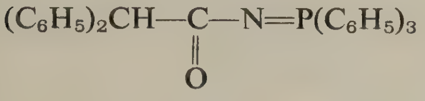
*Miscellaneous Methods*

*N*-Benzoyl triphenylphosphine imine can be made by heating $\alpha,\beta$-dibenzoyl hydroxylamine with triphenylphosphine[2121]:

$$PhCONHOCOPh + Ph_3P \rightarrow [PhCO_2^-Ph_3P^+NHCOPh] \rightarrow Ph_3P{=}NCOPh + PhCO_2H$$

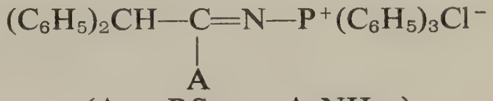
The chlorovinylphosphine imine **I** results from reaction of triphenylphosphine with chlorodiphenyl acetonitrile in an inert solvent.[2252] It reacts with methyl alcohol to form the acyl phosphine **II**[2252] and with mercaptans and amines to form the phosphonium salts **III**[2253]:

$$(C_6H_5)_2CCl.CN + (C_6H_5)_3P \rightarrow [(C_6H_5)_2CCN^-.(C_6H_5)_3P^+Cl] \rightarrow \underset{\textbf{I}}{(C_6H_5)_2C{=}CCl{-}N{=}P(C_6H_5)_3}$$



$$(C_6H_5)_2CH{-}\underset{\underset{O}{\|}}{C}{-}N{=}P(C_6H_5)_3$$

**II**



$$(C_6H_5)_2CH{-}\underset{\underset{A}{|}}{C}{=}N{-}P^+(C_6H_5)_3Cl^-$$

(A = RS— or ArNH—)

**III**

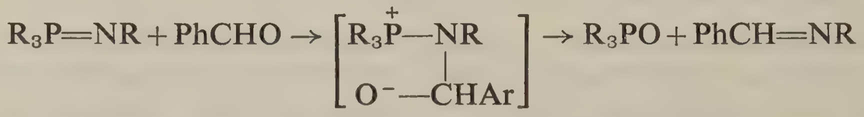
Aminophosphines, having the general structure $R_2PNHR'$ ($R = Ph$ or $OEt$; $R' = Ph$ or $Pr$), react with carbon tetrachloride or trichlorobromomethane to form phosphine imines $R_2PX{=}NR'$ ($X = Cl$ or $Br$) and chloroform.[2413]

Triphenylphosphine oxide, sulphide and *N*-phenylimide, and *O*,*O*,*O*-triethyl thiophosphate undergo trans-sulphonylimination by reaction with *N*-sulphinyl sulphonamides to form the corresponding *N*-sulphonyliminophosphorus derivatives[2352]:

$$RSO_2NSO + Ph_3PA \rightarrow Ph_3P{=}NSO_2R + ASO \qquad (A = O, S, NPh)$$
$$(EtO)_3PS + RSO_2NSO \rightarrow (EtO)_3P{=}NSO_2R + \text{‘}S_2O\text{’}$$

REACTIONS OF PHOSPHINE IMINES

Phosphine imines, like methylene phosphoranes, react with compounds containing an $A{=}O$ or $A{=}S$ group to form tertiary phosphine oxide or sulphide and a carbon compound having an $A{=}NR$ grouping. Examples of reactions are the conversion of isocyanates to carbodiimides, ketens to ketimines, carbon dioxide to isocyanate and carbon disulphide to isothiocyanate.[110,198] Kinetics of the reaction of $PhN{=}P(C_6H_4X)_3$ and $AC_6H_4N{=}PPh_3$ with benzaldehyde indicate that a betaine intermediate is involved. The rate-limiting step of the reaction changes, owing to variations of substituent A's affecting a delicate balance between the nucleophilicity of the nitrogen atom and the electrophilicity of the phosphorus atom[2293]:



$$R_3P{=}NR + PhCHO \rightarrow \left[\begin{array}{l} R_3\overset{+}{P}{-}NR \\ \quad\;\; | \qquad | \\ O^-{-}CHAr \end{array}\right] \rightarrow R_3PO + PhCH{=}NR$$

Some reactions of phosphine imines are indicated in Chart XXI.

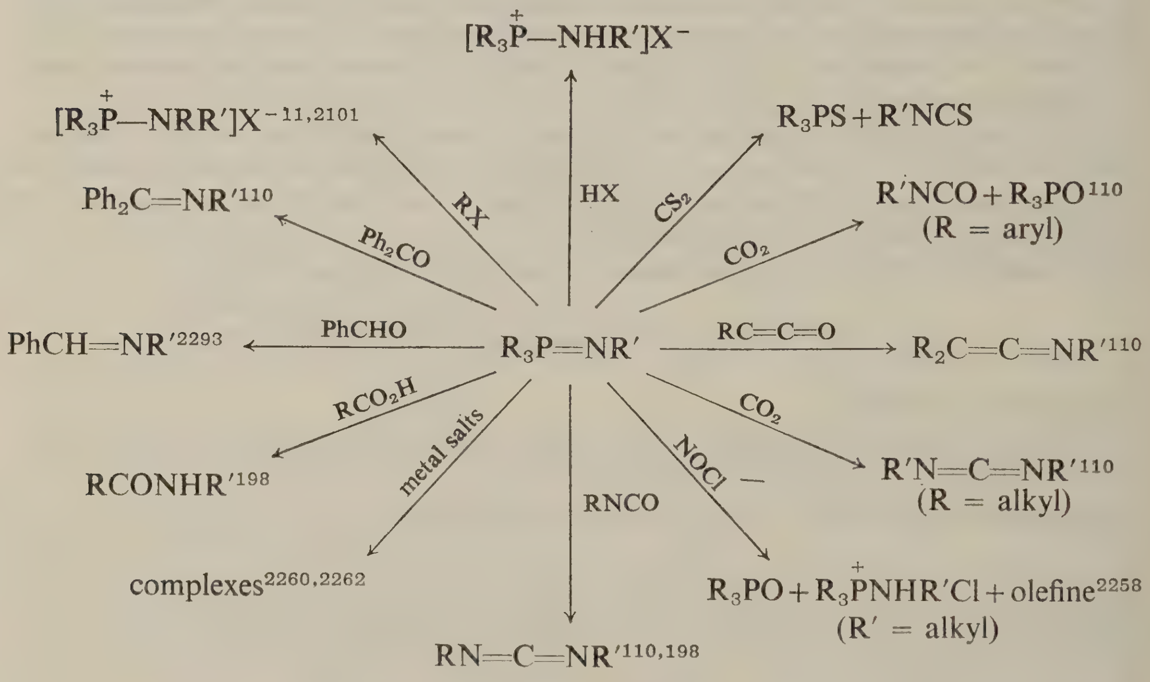


CHART XXI.—Reactions of phosphine imines

REACTION OF TRIVALENT PHOSPHORUS COMPOUNDS WITH AZIDES

Trivalent phosphorus compounds react with a wide variety of covalent azides to form complexes (phosphazides) which, in general, decompose at or below room temperature to nitrogen and an iminophosphorus compound:

$$A_1A_2A_3P + RN_3 \rightarrow [A_1A_2A_3P{=}N{-}N{=}N{-}R] \rightarrow A_1A_2A_3P{=}NR + N_2$$
$$(A_1A_2A_3 = \text{alkyl, aryl, alkoxy, halogen, hydrogen})$$

The rate of these reactions falls rapidly with diminishing nucleophilic character of the phosphorus atom, as for example along the series:

$$(R_2N)_3P > R_3P > Ar_3P > (MeO)_3P > (PhO)_3P > PCl_3(\text{zero at} \leqslant 35°)$$[110, 2266, 2270, 2273]

The effects of substituents on the phosphorus atom on the reaction of phenyl azide with $PA_3$ ($A = Cl$ or Ph) to form trichloro-*N*-phenylphosphine imine, dichlorophenyl-*N*-phenylphosphine imine, chlorodiphenyl-*N*-phenylphosphine imine and triphenyl-*N*-phenylphosphine imine are indicated below:

| *Reagents* | *Product* | *Reaction conditions* |
|---|---|---|
| $PCl_3 + PhN_3$ | $PhN{=}PCl_3$ | Reflux 3 days in benzene solution[2256] |
| $PhPCl_2 + PhN_3$ | $PhN{=}PCl_2Ph$ | Reflux 24 hr. in benzene solution[2256] |
| $Ph_2PCl + PhN_3$ | $PhN{=}PCl(Ph)_2$ | Reflux 2 hr. in benzene solution[2256] |
| $Ph_3P + PhN_3$ | $PhN{=}P(Ph)_3$ | Reacts violently at room temperature[110] |

Kinetic studies by Horner and Gross indicate a second-order reaction between triphenyl phosphine and *p*-substituted phenyl azides in xylene solution.[198] Electron-withdrawing groups like nitro increase the reaction rate and electron donating groups like dimethylamino decrease the reaction rate relative to phenyl azide. The kinetics indicate the rate of decomposition of the intermediate phosphazides to be greater than their rate of formation.

### *Phosphazides*

Phosphazides were reported by Staudinger to be very unstable compounds which can sometimes decompose explosively.[110, 177] In addition to the generally accepted structure **IV**, favoured by Staudinger, the existence of the isomeric form **V** has been considered by a number of authors. Evidence based largely on infra-red spectral analyses suggests that both forms can exist according to the nature of the R and R′ groups.[2189, 2256, 2266, 2271–2]

$$\underset{\textbf{IV}}{R_3P{=}N{-}N{=}N{-}R'} \qquad \underset{\textbf{V}}{R_3P{=}\overset{+}{N}(R')N{=}N^-}$$

Relatively few stable phosphazides have been isolated. They are yellow-coloured compounds which usually decompose at their melting point to the corresponding phosphine imine. Known compounds are of the type $R{-}N{=}N{-}N{=}PR'_3$: where R is strongly electron withdrawing as in *N*-(2,4,6-trinitrophenyl) triphenyl phosphazide,[2268] *N*-(*O*-carboxyphenyl) triphenyl phosphazide,[198] the *N*-(toluene-*p*-sulphonyl) phosphazides, $p\text{-}CH_3C_6H_4SO_2N{=}N{-}N{=}P(C_6H_5)_2X$ ($X = Ph, NHPh, N(C_3H_7)_2$) and the diphosphazide $PhN[P(Ph)_2{=}N{-}N{=}NSO_2C_6H_4CH_3\text{-}p]_2$[2269]; or where R′ is strongly electron releasing as in the amino-phosphazides, e.g., *N*-phenyl tris-(dipropylamino)phosphazide[2250] and *N*-phenyl tri-*iso*amyl phosphazide[110]; or where R is triphenylmethyl or 9-phenyl-9-fluorenyl and R′ is phenyl (very stable solids which undergo acid-catalyzed and iodine-catalyzed decomposition in polar solvents to the phosphine imine)[2189]; and the silicon compound $(C_6H_5)_3SiN{=}N{-}N{=}P(C_6H_5)_3$ which decomposes readily to *N*-(triphenylsilyl) triphenylphosphine imine.[2271]

### *Tertiary Phosphines*

There is a considerable volume of literature concerned with the reaction of tertiary phosphines (largely triphenyl phosphine) with organic azides to form *N*-substituted phosphine imines. Generally the reactants are mixed together in benzene solvent and the solution is heated until evolution of nitrogen ceases. Examples of the classes of azide which have been used are: alkyl[198, 2185] and aryl azides,[110, 177, 198] α-azido-carboxylic acids,[110, 198] benzoyl azide,[110] sulphonyl azides,[110, 2267, 2269] organosilicon azides,[2159, 2184, 2271] diarylphosphinyl and diarylthiophosphinyl azides,[2194, 2273] phenylphosphonyl and phenylthiophosphonyl diazides,[2274] diphenylcarbamyl azide,[2184] cyanogen azide,[2197] triphenylmethyl azide[2189] and alkyl and aryl diazides.[221] Although benzoyl azide and triphenylphosphine readily form the expected *N*-benzoyl triphenylphosphine imine,[110, 198, 2183] the analogous thio-compound from thiobenzoyl azide decomposes spontaneously to the phosphine sulphide and benzonitrile[198]:

$$\mathrm{PhCSN_3 + Ph_3P \rightarrow [Ph_3P{=}NCSPh] \rightarrow Ph_3PS + PhCN}$$

A useful route to *N*-hydrogen substituted phosphine imines is *via* the *N*-trimethylsilylphosphine imines. These readily lose the trimethylsilyl group on treatment with an alcohol containing a little sulphuric acid[2106, 2159, 2205]:

$$\mathrm{R_3P + Me_3SiN_3 \xrightarrow{-N_2} R_3P{=}NSiMe_3 \xrightarrow[ROH]{H^+} R_3P{=}NH}$$

This reaction fails when applied to *N*-trimethylsilyl dimethyldodecylphosphine imine; the product was found to be either dimethyl dodecylphosphine oxide or a bis-(phosphoranylidene) ammonium salt or a mixture of these two compounds[2255]:

$$\mathrm{RMe_2P{=}N{-}SiMe_3 \xrightarrow[H_2SO_4]{MeOH} RMe_2PO + [RMe_2P{=}N{=}PMe_2R]^+OMe^-}$$

Organotin, organogermanium and organosilicon nitrogen-substituted phosphine imines, iminophosphates and imidophosphoric amides (compounds $\mathrm{R_{4-n}M(N{=}PR'_3)_n}$; where R = alkyl, aryl; R′ = alkyl, aryl, alkoxyl, dialkylamino; M = Si, Ge, Sn) are made by reaction of the organometallic halide, sodium azide and appropriate trivalent phosphorus compound under anhydrous and anaerobic conditions[2160, 2194, 2273]:

$$\mathrm{PhSnCl_3 + 3NaN_3 + 3Ph_3P \rightarrow (Ph_3P{=}N)_3SnPh}$$
$$\mathrm{Ph_3SnCl + NaN_3 + (Me_2N)_3P \rightarrow Ph_3Sn{-}N{=}P(NMe_2)_3}$$
$$\mathrm{Bu_2GeCl_2 + 2NaN_3 + 2(MeO)_3P \rightarrow Bu_2Ge[N{=}P(OMe)_3]_2}$$

Diphenylphosphinyl chloride reacts similarly with triphenyl phosphine, but with diphenylthiophosphinyl chloride the reaction fails owing to formation of triphenylphosphine sulphide and diphenyl chlorophosphine which, in turn, reacts with sodium azide giving polymeric $\mathrm{Ph_2PN}$[2194, 2273]:

$$\mathrm{Ph_2POCl + NaN_3 + Ph_3P \rightarrow Ph_3P{=}NPOPh_2}$$
$$\mathrm{Ph_2PSCl + Ph_3P \rightarrow Ph_3PS + Ph_2PCl}$$
$$\mathrm{Ph_2PCl + NaN_3 \rightarrow (Ph_2PN)_n + N_2 + NaCl}$$

The reaction of triphenyl phosphine with diazidoquinones such as 2,3-diazido-1,4-naphthaquinone gives two products, the expected bisphosphine imine **VI** and the phosphorarylidine aminotriazole **VII**. The relative amounts of compounds of the type **VI** and **VII** formed are strongly influenced by the nature of the reaction solvent and the reacting phosphine. The triazole is the only compound isolated from $\mathrm{Bu_3P}$, $\mathrm{(C_5H_{10}N)_3P}$ and $\mathrm{PhP(C_5H_{10}N)_2}$.[2266]

Compound **VII**, in common with other negatively substituted phosphine imines, is highly resistant to hydrolysis.

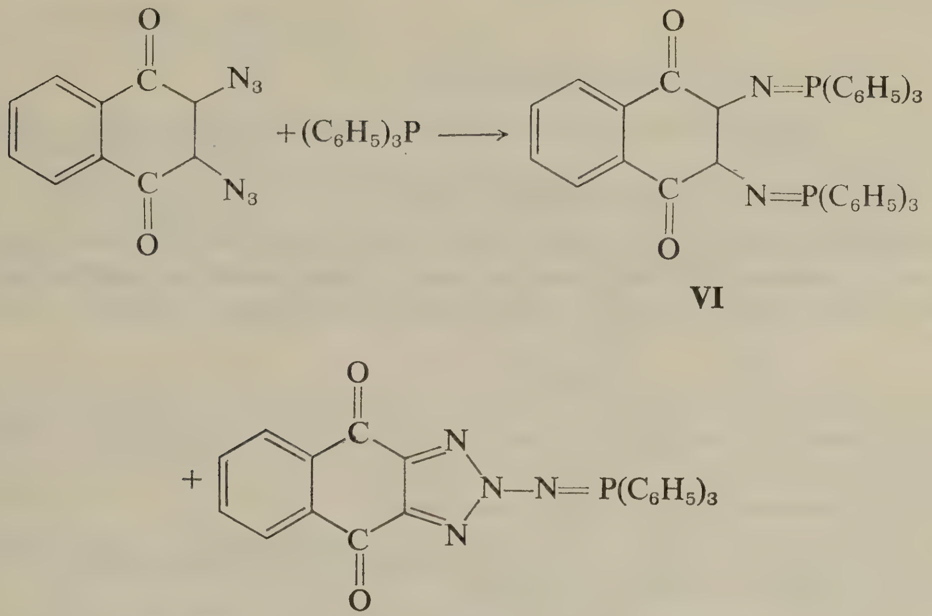
Phosphine led into an ether solution of phenyl azide does not react, on account of the low solubility of phosphine.[110] Phenyl phosphine and phenyl azide react violently with evolution of nitrogen.[110] The reaction of diphenylphosphine with triphenylsilyl azide involves addition and oxidation[2275]:

$$\mathrm{(C_6H_5)_3SiN_3 + (C_6H_5)_2PH \xrightarrow{-N_2} (C_6H_5)_3SiNH{-}P(C_6H_5)_2 \xrightarrow[-N_2]{(C_6H_5)_3SiN_3} (C_6H_5)_3SiNHP(C_6H_5)_2{=}NSi(C_6H_5)_3}$$

Tetraphenyl diphosphine forms the compound

$$\mathrm{(C_6H_5)_3SiN{=}P(C_6H_5)_2{-}P(C_6H_5)_2{=}NSi(C_6H_5)_3.}^{2275}$$

The reaction of hydrazoic acid with tertiary phosphines was studied by Staudinger[110] who formulated the products from $Ph_3P$ and $Et_3P$ as $Ph_3P{=}NH.HN_3$ and $Et_3P{=}NH.HN_3$ respectively. More recent work[2106, 2109] shows the triphenyl compound to be the phosphonium azide $Ph_3\overset{+}{P}NH_2N_3^-$.



**VI**

**VII**

*Halogenophosphines*

As indicated earlier, phosphorus trichloride and halogenophosphines react much more slowly with azide than the tertiary phosphines. Diphenyl chlorophosphine will react with phenyl azide,[2256, 2267] toluene-*p*-sulphonyl azide,[2267] and benzoyl azide[2198] to form *N*-substituted diphenyl phosphinimidic chlorides:

$$Ph_2PCl + RN_3 \rightarrow Ph_2PCl{=}NR \qquad (R = Ph, COPh, P\text{-}SO_2C_6H_4CH_3)$$

The *N*-phenyl compound is readily hydrolyzed to diphenyl phosphinic acid anilide[2294] and reacts with sodium azide to form *N*-phenyl azidodiphenyl phosphinous imide.[2267] Diphenyl chlorophosphine and hydrazoic acid react under photolytic conditions to form diphenyl phosphinimidic chloride, $Ph_2PCl{=}NH$, which readily undergoes dehydrochlorination to diphenyl phosphonitrile. A stable adduct $Ph_2PCl.HN_3$, m.p. 126°–126·5°, which is formed as a by-product in this reaction, was shown to have the isomeric phosphazide structure $Ph_2PCl{=}NH{-}N_2^-$.[2256]

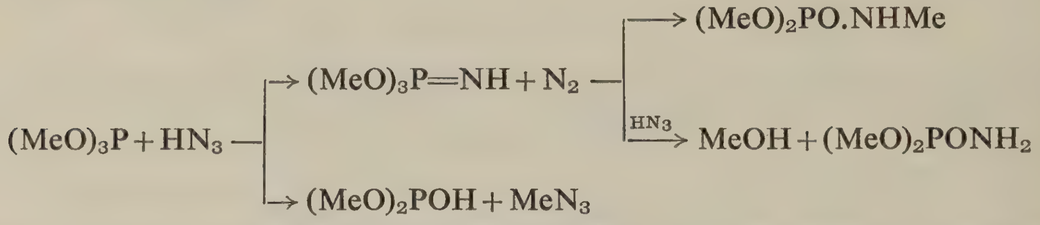
*Esters of Phosphorus(III) Acids*

Phosphorous acid triesters and organic azides readily form *N*-substituted phosphorimidic esters and nitrogen. Intermediates of the phosphazide type have not been isolated. The reaction may be written in the general form:

$$(RO)_3P + R'N_3 \rightarrow (RO)_3P{=}NR' + N_2$$

(where $R'N_3$ = alkyl azide or aryl azide,[2200, 2241] alkyl or aryl sulphonyl azides and aliphatic disulphonyl azides,[2199] acyl azides,[2196, 2198, 2241] dialkoxyphosphinyl azides,[2201–3] diarylphosphonyl azide[2194]; R = alkyl, aryl). Similar reactions have been demonstrated in using diesters of phosphonous acids[2196, 2241, 2303] to form *N*-substituted phosphonimidic esters $(RO)_2PR'{=}NR''$, esters of phosphinous[2303] acid to form *N*-substituted phosphinimidic esters $ROPR'_2{=}NR''$, and between trialkyl phosphorotrithioites and aliphatic $\alpha$-$\omega$-disulphonyl azides to form *N*-substituted phosphorimidic trithioates $(RS)_3P{=}NSO_2R'$.[2199] The reaction rate of compounds $(RA)_3P$ with sulphonyl azides decreases in the series: RA = EtO > EtS > PhO > PhS.[2199]

Hydrogen azide and trimethyl phosphite interact slowly at room temperature to form a mixture of dimethyl phosphoramidate, *N*-methyl dimethyl phosphoramidate and dimethyl phosphite[2201]:

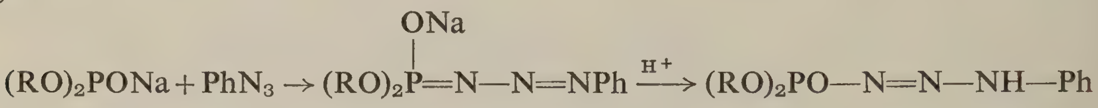


$$(MeO)_3P + HN_3 \rightarrow (MeO)_3P{=}NH + N_2 \rightarrow (MeO)_2PO.NHMe$$

$$(MeO)_3P{=}NH + N_2 \xrightarrow{HN_3} MeOH + (MeO)_2PONH_2$$

$$(MeO)_3P + HN_3 \rightarrow (MeO)_2POH + MeN_3$$

Salts of dialkyl hydrogen phosphites, but not the phosphites themselves, react with phenyl azide giving salts of dialkoxyphosphinyl triazine, which on acidification yield the free triazines. These are yellow solids which decompose on melting, losing nitrogen[2204]:



$$(RO)_2PONa + PhN_3 \rightarrow (RO)_2\overset{ONa}{\overset{|}{P}}{=}N{-}N{=}NPh \xrightarrow{H^+} (RO)_2PO{-}N{=}N{-}NH{-}Ph$$

REACTIONS OF PHOSPHORIMIDIC ESTERS AND AMIDES

Mild hydrolysis of trialkyl *N*-substituted phosphorimidates yields the corresponding *N*-substituted phosphoramidates:

$$(RO)_3P{=}NR' \xrightarrow{H_2O} (RO)_2PO.NHR' + ROH$$

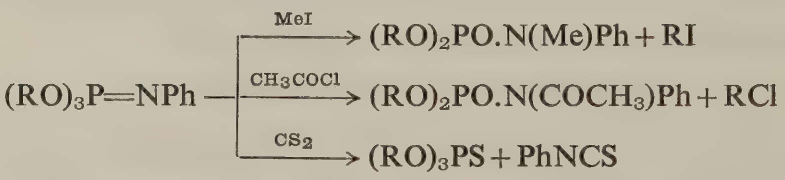
The stability towards hydrolysis is increased when the nitrogen atom carries electron-withdrawing groups such as alkyl/aryl sulphonyl or diaryl phosphinyl. Thus, when R′ is phenyl the compounds are slowly hydrolyzed by water[2200, 2232]; when R′ is acyl hydrolysis can be effected by boiling with water or treating with dilute alkali [2216–7, 2222]; when R′ is alkyl/aryl sulphonyl the compounds are hydrolyzed by heating with aqueous sodium hydroxide to form salts of the phosphoramidate which on acidification yield the free phosphoramidate[2212, 2223, 2288]:

$$RSO_2N{=}P(OR)_3 \xrightarrow{NaOH} [RSO_2N{-}PO(OR)_2]^- Na^+ \xrightarrow{H^+} RSO_2NHPO(OR)_2$$

Amides such as triaryl arylsulphonyl phosphorimidic triamide $ArSO_2N{=}P(NHAr)_3$ are remarkably stable to hydrolysis, even with hot alcoholic sodium hydroxide.[2219] In contrast triaryl aroyl phosphorimidic triamides $ArCON{=}P(NHAr)_3$ hydrolyze very readily on heating with aqueous alcohol or on exposure to water vapour to form diaryl aroyl phosphoric triamides $ArCONHPO(NHAr)_2$.[2234] The same products, together with aryl benzamide, are formed by heating with benzoic acid in pyridine solution:

$$ArCON{=}P(NHAr)_3 + PhCO_2H \rightarrow ArCONHPO(NHAr)_2 + PhCONHAr$$

Reactions of trialkyl *N*-phenyl phosphorimidates with methyl iodide, acetyl chloride and carbon disulphide are indicated below[2200]:

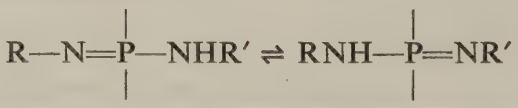


$$(RO)_3P{=}NPh \xrightarrow{MeI} (RO)_2PO.N(Me)Ph + RI$$

$$(RO)_3P{=}NPh \xrightarrow{CH_3COCl} (RO)_2PO.N(COCH_3)Ph + RCl$$

$$(RO)_3P{=}NPh \xrightarrow{CS_2} (RO)_3PS + PhNCS$$

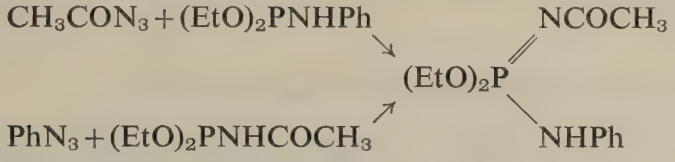
The existence of tautomerism:



$$R{-}N{=}\overset{|}{\underset{|}{P}}{-}NHR' \rightleftharpoons RNH{-}\overset{|}{\underset{|}{P}}{=}NR'$$

in phosphoramidimidic esters has been demonstrated by Kabachnik from infra-red studies. The position of equilibrium depends on the electrophilic nature of R and R′.

[2196] Supporting evidence for the tautomerism is the formation of a single compound diethyl phosphor-*N*-phenylamido-*N*-acetyl imidate from the two reactions indicated below[2196]:



*Reaction of Amino Compounds with Pentavalent Phosphorus Halides*

The reactions of phosphorus pentachloride and halogenophosphoranes with amino-compounds, especially amides, has been extensively investigated by Kirsanov and co-workers.[2278] Phosphorus pentachloride forms an *N*-substituted phosphorimidic trichloride (the trichlorophosphazo compounds of Kirsanov):

$$RNH_2 + PCl_5 \rightarrow RN{=}PCl_3 + 2HCl$$

The reactions are generally carried out in inert solvent at ambient or somewhat elevated temperature with rigorous exclusion of moisture. Examples of amino-compounds which have been used in the reaction are: aromatic amines,[2226, 2232] carboxylic acid amides[2211, 2214, 2218, 2296] and diamides,[2245] alkyl and aryl sulphonamides,[2209, 2289-91] urea,[2211] *N,N*-diphenyl urea,[2221] esters of oxamic acid,[2211, 2213, 2416] urethanes,[2211, 2229, 2242] sulphamide,[2203, 2209, 2246, 2259] amidines such as *N*-arylsulphonyl benzamidine,[2225] and phosphorus amides such as diphenyl phosphoramide[1718, 2220] and diphenyl phosphoroamidothionate.[2220] Bifunctional amino compounds such as urea, sulphamide and *p*-aminobenzene sulphonamide[2276] react with two equivalents of phosphorus pentachloride giving bis-phosphorimidic trichlorides $Cl_3P{=}N{-}A{-}N{=}PCl_3$. Oxamic esters react according to the equation[2213]:

$$RO_2CCONH_2 + PCl_5 \rightarrow POCl_3 + ROCCl_2CONH_2 \xrightarrow{PCl_5} ROCCl_2CON{=}PCl_3$$

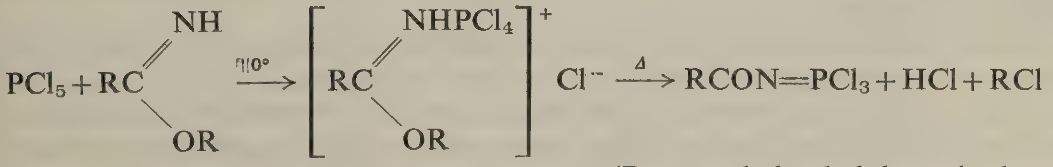
*Variation of the Phosphorus Component*

Aryl tetrachlorophosphoranes,[2227-31, 2233, 2277] diaryl trichlorophosphoranes,[1718, 2190, 2230-1, 2236, 2248, 2302] triaryl dihalogenophosphoranes[2190] and triarylphosphite dihalides[1718] react like phosphorus pentachloride with amino-compounds to form *P*-substituted phosphorus imines. Examples are: the formation of *N*-aryl phenylphosphonimidic dichlorides $ArN{=}PPhCl_2$ from aromatic amines and $PhPCl_4$[2233]; *N*-(toluene-*p*-sulphonyl)phenylphosphorimidic dichloride, $p\text{-}CH_3C_6H_4SO_2N{=}PC_6H_5.Cl_2$, from toluene *p*-sulphonamide[2227]; *N*- carbethoxy diphenylphosphinimidic chloride, $RO_2CN{=}P(C_6H_5)_2Cl$, from urethane and $Ph_2PCl_3$[2190]; and triphenyl *N*-aryl phosphorimidates $ArN{=}P(OPh)_3$ from $(PhO)_3PCl_2$ and aromatic amines.[1718] Diphenyl trichlorophosphorane and aromatic amine hydrochlorides form the quasiphosphonium salts $[ArNHP(C_6H_5)_2Cl]^+Cl^-$ which on treatment with pyridine yield the *N*-aryl diphenylphosphinimidic chloride $ArN{=}P(C_6H_5)_2Cl$.[2236]

Pentaphenoxy phosphorane reacts in a manner analogous to phosphorus pentachloride with aromatic amines and amides giving triphenyl *N*-substituted phosphorimidates[1718]:

$$(PhO)_5P + RNH_2 \rightarrow 2PhOH + (PhO)_3P{=}NR \qquad (R = Ph, (PhO)_2PO, (PhO)_2PS)$$

Imino-esters or their hydrochlorides react with phosphorus pentachloride at 0°C. to form ionic adducts which, on moderate heating, decompose to the *N*-acyl phosphorimidic trichloride[2277, 2279, 2281]:



(R = methyl, ethyl, benzyl, phenyl)

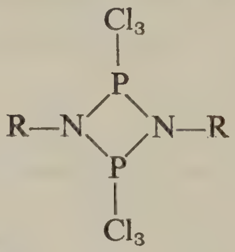
Removal of hydrogen chloride during the reaction is essential in the preparation of *N*-benzoyl phenylphosphonimidic dichloride from $PhPCl_4$ and methyl benzimino ether to prevent decomposition of the product to benzonitrile and phenyl phosphonyl dichloride.[2277]

### PROPERTIES AND REACTIONS OF PHOSPHORUS IMIDIC HALIDES

*N*-Substituted phosphorimidic chlorides are generally crystalline moisture-sensitive solids which can be crystallized from inert organic solvents. The *N*-methyl and *N*-chloromethyl compounds (**IX**: $R = CH_3$ or $CH_2Cl$) are dimeric in solution.[2224, 2239–40] Aromatic amines or their hydrochlorides react with phosphorus pentachloride in benzene solution to form either the momomeric *N*-aryl phosphorimidic trichloride **VIII**, or the dimer **IX**.

$RN{=}PCl_3$

**VIII**



**IX**

Aromatic amines having $K_b$ in the range $10^{-9}$ to $10^{-13}$ yield dimeric products, whilst amines of lower basicity yield monomers. Products derived from amines with $K_b$ $10^{-9}$ to $10^{-10}$ do not dissociate in benzene solution; those from amines with lower basicity dissociate in solution but the monomers cannot be isolated owing to dimerization which occurs when the solvent is evaporated. Derivatives of the low basicity amines are low melting-point solids which in chemical and physical behaviour resemble the monomeric *N*-acyl and *N*-sulphonyl compounds; they react with formic acid giving *N*-aryl phosphoramidic dichlorides. The dimeric compounds differ from the monomers in physical properties and chemical behaviour; they are high melting-point solids which react with formic acid giving chlorine-free glassy solids.[2226, 2232] The tendency of compounds of this type to dimerize is greatly reduced by replacing chlorine by aryl groups as in $PhN{=}PCl_2Ph$.[2223]

Mild hydrolysis of phosphorimidic trichlorides with water vapour, one equivalent of formic acid[2211, 2213, 2221, 2225, 2232, 2291] or with water in acetone[2215] gives the *N*-substituted phosphoramidic dichloride; similarly phosphonimidic dichlorides give the phosphonamidic chloride and phosphinimidic chlorides the phosphinamidate[2236, 2304]:

$$RN{=}PCl.R'R'' \xrightarrow[-CO,\ -HCl]{HCO_2H} RNH{-}PO.R'R'' \qquad (R', R'' = \text{halogen, alkyl, aryl})$$

Further hydrolysis with excess of water gives the phosphorus acid, amine and hydrochloric acid. *N*-(Diphenoxyphosphinyl) phosphorimidic trichloride $(PhO)_2PO.N{=}PCl_3$[2200] is hydrolyzed to *N*-(diphenoxyphosphinyl) phosphoramidic acid $(PhO)_2PO.NHPO_3H_2$ which is unusually stable to boiling water. This is attributed to hydrogen-bonding of the acidic group to the adjacent phosphoryl bond. In contrast, *N*-(diphenoxythionophosphinyl)phosphorimidic trichloride $(PhO)_2PS.N{=}PCl_3$ is readily hydrolyzed with water to orthophosphoric acid and diphenyl phosphoramidothionate.[2220]

*N*-Acyl phosphorimidic trichlorides decompose to phosphoryl chloride and a nitrile at temperatures near 100°C., and at lower temperatures in the presence of dry hydrogen chloride or phosphorus oxychloride.[2209, 2211, 2214, 2222, 2277] Introduction of aryl or aryloxy-groups on the phosphorus atom or electronegative substituents on the acyl group raises the decomposition temperatures of the pure compounds. Thus

*N*-benzoyl triphenyl phosphine imine decomposes at *ca.* 200° [2235]; *N*-trichloroacetyl phosphorimidic trichloride, $Cl_3CCON{=}PCl_3$, decomposes to phosphorus oxychloride and trichloroacetonitrile at 260° when pure and at 205°–210° in the presence of gaseous hydrogen chloride[2296]:

$$RCON{=}PCl_3 \xrightarrow{\Delta} RCN + POCl_3$$

*N*-Carbethoxyphosphorimidic trichlorides decompose at *ca.* 45° giving ethyl chloride and isocyanatophosphoryl dichloride[2211, 2242]:

$$EtOCON{=}PCl_3 \rightarrow EtCl + OCNPO.Cl_2$$

Some reactions of *N*-alkyl/aryl sulphonylphosphorimidic trichlorides are indicated in Chart XXII. Similar reactions have been carried out using *N*-acyl phosphorimidic trichlorides,[2215-8, 2222, 2234-5] *N*-diaryl phosphonyl phosphorimidic trichlorides[2220] and with *N*-substituted phosphonimidic and phosphinimidic halides.[2228-31, 2247, 2249]

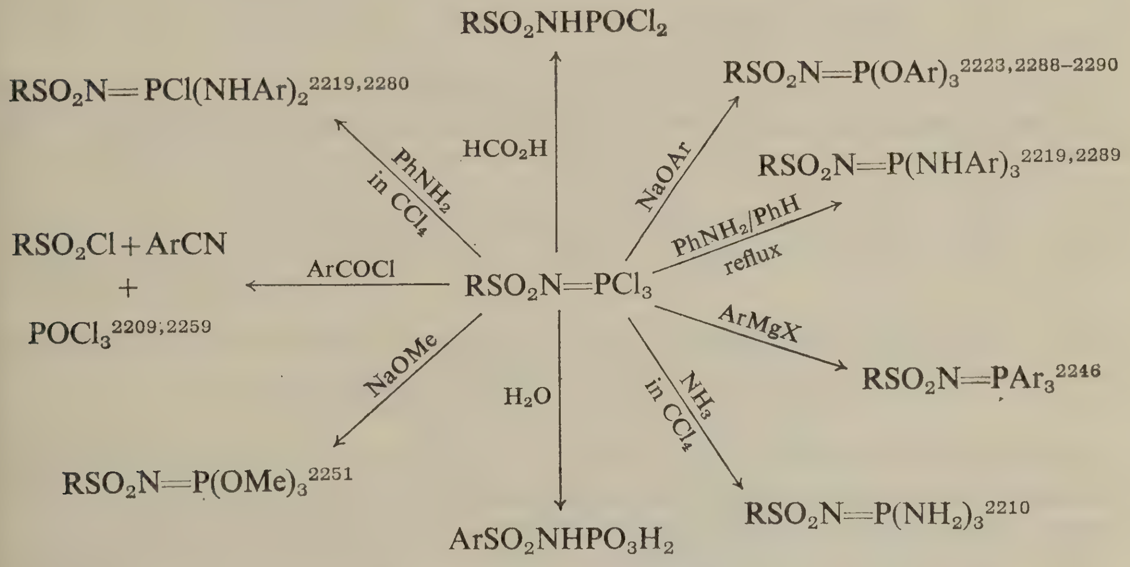


CHART XXII.—Reactions of *N*-sulphonylphosphorimidic trichlorides

### N-*Chloro Compounds and Tervalent Phosphorus Compounds*

Triaryl phosphines and chloramine-*T* react in anhydrous alcoholic solution to form *N*-(toluene-*p*-sulphonyl)triarylphosphine imines; trialkylphosphines behave similarly but the imine products are difficult to isolate[2287]:

$$ArSO_2NNaCl + PAr_3 \rightarrow ArSO_2N{=}PAr_3 + NaCl$$

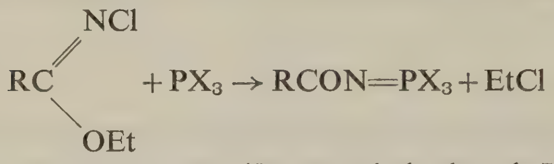
Trialkyl *N*-(toluene sulphonyl)phosphoramidate can be prepared similarly from trialkyl phosphite and chloramine-*T* in carbon tetrachloride solution.[637, 2212] In the presence of water the phosphite is oxidized by chloramine-*T* to triethyl phosphate.[637]

Phosphorus trichloride[2238] and tribromide[2237] react exothermically with chloramine-*T* in carbon tetrachloride to form the corresponding *N*-(toluene-*p*-sulphonyl)-phosphorimidic trihalides. In the absence of solvent the reaction is explosive. Phosphorus pentachloride and chloramine-*T* react under similar conditions to form chlorine and the phosphorimidic trichloride.[2243] *N,N*-Dichloroaryl sulphonamides react with phosphorus trichloride, aryl halogenophosphines and triarylphosphines in benzene solution at reflux temperatures to form *N*-(arylsulphonyl)phosphine imines[2302-3]:

$$ArSO_2N.NaCl + PX_3 \rightarrow ArSO_2N{=}PX_3 + NaCl \qquad (X = Cl, Br)$$
$$ArSO_2NCl_2 + PAr_nCl_{3-n} \rightarrow ArSO_2N{=}PAr_nCl_{(3-n)} + Cl_2 \qquad (n = 0, 1, 2, 3)$$
$$ArSO_2N,NaCl + PCl_5 \rightarrow ArSO_2N{=}PCl_3 + Cl_2 + NaCl$$

Compounds of the type $RSO_2N{=}POR'.X_2$ (R = alkyl, aryl; R′ = alkyl; X = F, Cl) are made by heating *N*,*N*-dichlorosulphonamides with alkyl phosphorodifluoridites or alkyl phosphorodichloridites.[2286]

Triphenylphosphine, halogenophenyl phosphines and triaryl phosphites have been shown to react in inert solvents with *N*-chloroimino ethers to form *N*-acyl phosphorus imines,[2191, 2282–3] and with diethyl chloriminocarbonate[2192–3] or with *N*,*N*-dichlorourethanes[2190] to form *N*-carbethoxy-phosphorus imines:



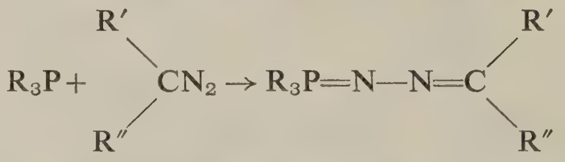
$$RC({=}NCl)OEt + PX_3 \rightarrow RCON{=}PX_3 + EtCl$$

(R = methyl, phenyl; X = phenyl, phenoxy, chlorine, cyano)

$$(EtO)_2C{=}NCl + PX_3 \rightarrow EtOCON{=}PX_3 \qquad (X = Ph, Cl, alkyl, OPh)$$
$$EtOCONCl_2 + (C_6H_5)_3P \rightarrow EtOCON{=}P(C_6H_5)_3$$

*Phosphazines*

Phosphazines were first prepared by Staudinger and co-workers[110, 177, 2292] by the reaction of tertiary phosphines with aliphatic diazo compounds[189, 2018, 2102–3, 2353]:



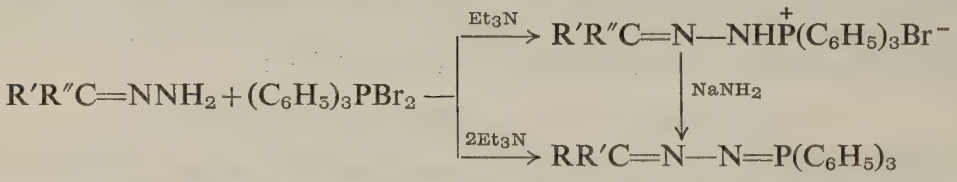
$$R_3P + R'R''CN_2 \rightarrow R_3P{=}N{-}N{=}CR'R''$$

Ortho- and para-quinone azides react like aliphatic diazo-compounds with triphenylphosphine giving quinone triphenyl phosphazines, e.g.,

$$p\text{-}O{=}C_6H_4{=}N{-}N{=}P(C_6H_5)_3{}^{1996,\,2295}$$

A kinetic study of the reaction of $p$-$XC_6H_4P(C_6H_5)_2$ with 9-diazofluorene in benzene solution to form aryldiphenyl-9-fluorenyl phosphazine shows the reaction to be of second order. Electron donating groups X enhance the reaction rate.[2206]

The range of known phosphazines has been considerably extended by Bestmann [2102, 2181] who allowed hydrazones to react with triphenyl dibromophosphorane in the presence of triethylamine. The intermediate $N^{\beta}$-alkylidene hydrazino-phosphonium salts may be prepared by using one equivalent of the amine; they have been converted to the phosphazines using sodamide in liquid ammonia[2254]:



$$\begin{tikzcd}
 & R'R''C{=}N{-}NH\overset{+}{P}(C_6H_5)_3Br^- \arrow[d, "NaNH_2"] \\
R'R''C{=}NNH_2 + (C_6H_5)_3PBr_2 \arrow[ur, "Et_3N"] \arrow[r, "2Et_3N"'] & RR'C{=}N{-}N{=}P(C_6H_5)_3
\end{tikzcd}$$

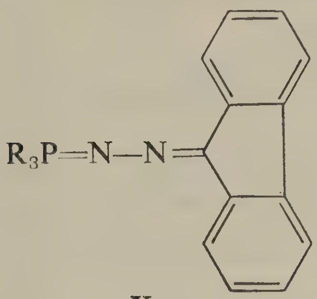
An alternative approach is the condensation of ketones with *N*-amino-triphenylphosphine imine which can be readily obtained by the action of strong bases on triphenyl hydrazine phosphonium salts[2414]:

$$Ph_3PBr_2 + N_2H_4 \xrightarrow{Et_3N} Ph_3\overset{+}{P}NHNH_2Br^-$$
$$Ph_3\overset{+}{P}NHNH_2Br^- \xrightarrow[R_2CO]{BuLi} Ph_3P{=}N{-}N{=}CR_2$$

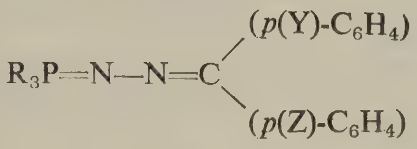
Phosphazines are a reactive class. Most compounds reported are solids, which, when R is phenyl, are generally stable under ambient conditions. Thermal decomposition can proceed either with loss of nitrogen to form a methylene phosphorane[177, 189, 2353] or to give tertiary phosphine and aliphatic diazo compounds depending on the nature of R, R′ and R″[2102]:

$$Ph_3P{=}N{-}N{=}CPh_2 \xrightarrow{\Delta} Ph_3P{=}CPh_2$$

The basicity and reactivity of phosphazines as nucleophiles depends on the inductive and mesomeric effects of the R, R′ and R″ groups.[2102] *P*-Triethyl compounds are strong bases, *P*-triphenyl compounds weak.[177] Dipole moments and molecular spectra of the triaryl phosphazines types **X** and **XI** have been interpreted as indicating a merocyanine-like mesomerism in the compounds[2301]:



**X**

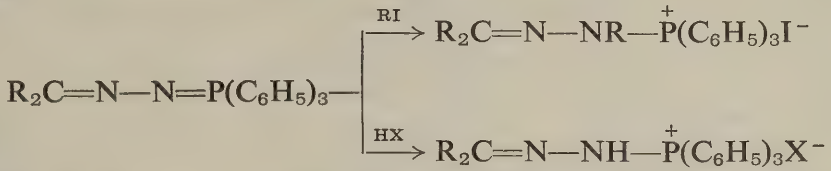


**XI**

Simple phosphazines such as formaldehyde triphenylphosphazine,

$$CH_2{=}N{-}N{=}P(C_6H_5)_3$$

and benzylidene triphenylphosphazine react with hydrogen halides or with alkyl halides to form $N^\beta$-alkylidene hydrazinophosphonium salts and $N^\beta$-alkylidene-$N^\alpha$-alkyl hydrazinophosphonium salts respectively.[2102, 2254] α-Keto phosphazines, formed from diazoketones and tertiary phosphines,[2103] react with methyl iodide accompanied by P–N bond fission to form the diazoketone and a normal phosphonium salt[2102-3]:

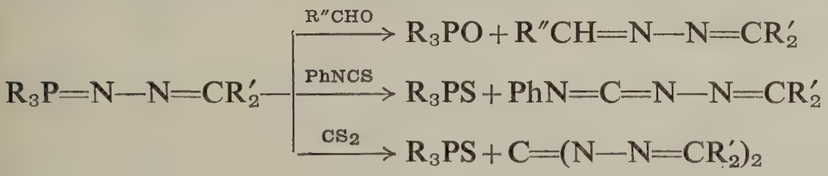


$$R_2C{=}N{-}N{=}P(C_6H_5)_3 \begin{cases} \xrightarrow{RI} R_2C{=}N{-}NR{-}\overset{+}{P}(C_6H_5)_3I^- \\ \xrightarrow{HX} R_2C{=}N{-}NH{-}\overset{+}{P}(C_6H_5)_3X^- \end{cases}$$

Phosphazines derived from quinone azides react with aqueous hydrochloric acid giving hydroxyaryl azotriphenylphosphonium chlorides, e.g.,

$$p\text{-}HOC_6H_4N{=}N{-}\overset{+}{P}(C_6H_5)_3Cl^{-}$$ [1996]

Phosphazines react with a variety of unsaturated oxygen and sulphur-containing compounds such as aldehydes,[2181] ketenes,[177, 2181] isocyanates,[177] carbon disulphide,[2292] phenyl isothiocyanate[177] and sulphur dioxide[2292] to form tertiary phosphine oxide/sulphide and an organic hydrazine derivative. They are readily hydrolyzed, particularly in basic media, to hydrazone and tertiary phosphine oxide[177]:



$$R_3P{=}N{-}N{=}CR'_2 \begin{cases} \xrightarrow{R''CHO} R_3PO + R''CH{=}N{-}N{=}CR'_2 \\ \xrightarrow{PhNCS} R_3PS + PhN{=}C{=}N{-}N{=}CR'_2 \\ \xrightarrow{CS_2} R_3PS + C{=}(N{-}N{=}CR'_2)_2 \end{cases}$$

Trialkyl phosphites react readily with diazomethane to form liquid trialkyl phosphorazines which can be distilled under vacuum.[2207] They react vigorously with carbon disulphide giving trialkyl phosphorothionates:

$$(RO)_3P + CH_2N_2 \rightarrow (RO)_3P{=}N{-}N{=}CH_2 \xrightarrow{CS_2} (RO)_3PS$$

Tri-*iso*propyl phosphite and diphenyl diazomethane give a quantitative yield of benzophenone tri-*iso*propyl phosphorazine which on hydrolysis, in contrast to the behaviour of phosphazines, gives propylene and *N*-diphenylmethylene phosphorohydrazidate[2208]:

$$Ph_2C{=}N{-}N{=}P(OC_3H_7)_3 \rightarrow C_3H_7 + Ph_2C{=}N{-}NHPO(OC_3H_7)_2$$

**Refs. p. 1082**

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# SECTION XXXIV

# THE SPECTROSCOPY AND STRUCTURE OF PHOSPHORUS AND PHOSPHORUS COMPOUNDS

BY A. C. CHAPMAN

## ELEMENTAL PHOSPHORUS

### Atomic and Ionized Phosphorus

EMISSION SPECTRA

THE visible, ultra-violet,[52–6, 59–65, 67, 800–3] and far ultra-violet[57–8, 800–2] emission spectra of atomic phosphorus in various degrees of ionization up to P XIII have been investigated. References are as follow: P I,[61, 63] P II,[59, 62–4, 800, 812] P III,[55–6, 62, 64, 801, 811] P IV,[56, 62, 64, 802, 811, 817] P V,[52–3, 60, 62, 65, 67] P VI–XII,[65, 812] P XIII.[803] The use of the spectra for analytical purposes has been discussed.[67–71] Many of the spectral data are contained in published tables.[72–4, 804] Table I gives a list of the principal lines in the spectra of phosphorus; the data are taken from References 62, 63, 801 and 817 for lines of P III–P V and for wave-lengths below 2000 A., and from Reference 73 for the remainder. The electric-field gradients at the nucleus for various states of atomic phosphorus have been calculated from the spectra.[814] The excitation of forbidden lines between the sub-levels of the ground state has been studied.[948]

*Table I.—Emission Spectra of Phosphorus*(a)

| Wave-length A. | Intensity | | | Wave-length A. | Intensity | | |
|---|---|---|---|---|---|---|---|
| | Arc | Spark | Geissler tube | | Arc | Spark | Geissler tube |
| V 255·596 | | 7 | | II 1452·949 | | | 12 |
| V 255·688 | | 7 | | IV 1484·506 | | 6 | |
| V 390·700 | | 8 | | II 1488·530 | | | 12 |
| V 475·610 | | 8 | | II 1532·558 | | | 12 |
| V 542·567 | | 7 | | II 1535·955 | | | 12 |
| V 544·914 | | 8 | | II 1536·459 | | | 12 |
| IV 631·790 | | 10 | | II 1542·321 | | | 15 |
| V 673·888 | | 10 | | II 1543·144 | | | 12 |
| IV 756·510 | | 6 | | I 1674·661 | | | 12 |
| IV 823·181 | | 20 | | I 1679·730 | | | 12 |
| IV 824·726 | | 20 | | I 1685·957 | | | 11 |
| IV 827·932 | | 25 | | I 1774·942 | | | 12 |
| III 859·668 | | 8 | | I 1782·830 | | | 12 |
| V 865·435 | | 15 | | I 1787·686 | | | 12 |
| V 871·396 | | 15 | | I 1858·924 | | | 12 |
| IV 875·132 | | 11 | | I 1859·401 | | | 12 |
| IV 877·493 | | 11 | | IV 1888·652 | | 10 | |
| IV 950·662 | | 25 | | I 2024·546 | 15 | | 12 |
| III 998·000 | | 8 | | I 2032·447 | 12 | | 15 |
| III 1003·592 | | 10 | | I 2033·489 | 15 | | 20 |
| IV 1030·511 | | 10 | | I 2135·466 | 12 | | 20 |
| IV 1033·099 | | 8 | | I 2136·199 | 15 | | 25 |
| IV 1035·505 | | 8 | | I 2149·108 | 15 | | 25 |
| V 1117·979 | | 15 | | I 2152·950 | 12 | | 25 |
| V 1128·006 | | 10 | | I 2154·081 | 15 | | 25 |

*Table I.—(continued)*

| Wave-length A. | Intensity |  |  | Wave-length A. | Intensity |  |  |
|---|---|---|---|---|---|---|---|
|  | Arc | Spark | Geissler tube |  | Arc | Spark | Geissler tube |
| I 2235·734 | 10 |  | 1 | 4178·36 |  |  | 300 |
| V 2440·75 |  | 5 |  | 4222·15 | 300 |  | 150 |
| II 2497·328 |  |  | 100 | III 4223·34 |  | 7 |  |
| I 2534·01 P | 50 |  | 20 | 4246·88 | 70 |  | 150 |
| I 2535·65 P | 100 |  | 30 | III 4247·87 |  | 7 |  |
| I 2553·28 P | 80 |  | 20 | 4249·57 |  |  | 100 |
| I 2554·93 P | 60 |  | 20 | 4385·33 |  |  | 100 |
| III 2611·05 |  | 6 |  | 4414·28 |  |  | 100 |
| III 2632·62 |  | 6 |  | II 4452·44 |  |  | 150 |
| III 3978·27 |  | 7 |  | II 4475·26 |  |  | 150 |
| IV 2740·13 |  | 5 |  | II 4499·17 |  |  | 150 |
| III 2884·75 |  | 5 |  | II 4530·78 |  |  | 150 |
| III 2896·17 |  | 5 |  | II 4554·80 |  |  | 100 |
| V 3175·14 |  | 5 |  | II 4558·03 |  |  | 100 |
| 3219·30 |  |  | 100 | II 4565·21 |  |  | 100 |
| III 3220·23 |  | 6 |  | II 4587·90 |  |  | 300 |
| III 3234·54 |  | 6 |  | II 4589·78 |  |  | 300 |
| II 3308·85 |  |  | 100 | II 4601·96 |  |  | 300 |
| IV 3348·67 |  | 6 |  | II 4658·11 |  |  | 100 |
| 3364·43 |  |  | 100 | II 4678·94 |  |  | 100 |
| IV 3365·39 |  | 6 |  | 4727·46 |  |  | 100 |
| IV 3372·06 |  | 5 |  | II 4943·41 |  |  | 150 |
| II 3419·24 |  |  | 100 | II 4969·64 |  |  | 150 |
| II 3424·87 |  |  | 100 | II 5191·40 |  |  | 100 |
| II 3507·36 |  |  | 100 | II 5253·48 |  |  | 300 |
| II 3556·48 |  |  | 100 | II 5296·09 |  |  | 300 |
| 3617·09 |  |  | 100 | II 5316·07 |  |  | 150 |
| 3653·38 |  |  | 100 | 5344·72 |  |  | 150 |
| II 3664·19 |  |  | 100 | 5386·87 |  |  | 150 |
| II 3676·26 |  |  | 100 | II 5409·65 |  |  | 150 |
| II 3706·05 |  |  | 150 | II 5425·92 |  |  | 150 |
| 3802·07 |  |  | 100 | II 5450·65 |  |  | 100 |
| II 3827·44 |  |  | 150 | 5460·85 |  |  | 100 |
| 3885·17 |  |  | 150 | II 5499·71 |  |  | 150 |
| 3895·02 |  |  | 100 | II 6043·05 |  |  | 150 |
| 3904·78 |  |  | 100 | I 9525·78 | 100 |  |  |
| 3914·26 |  |  | 100 | I 9545·27 | 20 |  |  |
| 3957·62 |  |  | 100 | I 9563·45 | 25 |  |  |
| III 3978·27 |  | 8 |  | I 9593·54 | 70 |  |  |
| II 4044·49 |  |  | 150 | I 9734·74 | 50 |  |  |
| 4059·27 |  |  | 100 | I 9750·73 | 70 |  |  |
| III 4060·41 |  | 6 |  | I 9796·79 | 100 |  |  |
| 4080·04 |  |  | 150 | I 9903·74 | 18 |  |  |
| III 4081·18 |  | 7 |  | I 9976·65 | 10 |  |  |

(a) Persistent lines are indicated by P I, II, III, etc., and indicate lines classified as emitted by neutral, singly ionized, doubly ionized, etc., atoms respectively.

Wave-lengths below 2000 A. refer to vacuum and those above 2000 A. refer to air. Intensities of lines below 2000 A. and from P III–V are on an arbitrary scale; the remainder are on a scale of 9000.

### PARAMAGNETIC RESONANCE SPECTRA

The paramagnetic resonance spectrum of the ground state ($^4S_{3/2}$) of atomic phosphorus gives a *g*-value for the ground state of 2·0019 ± 0·0004, and shows a narrow doublet (separation 56·2 Mc/s) arising from a magnetic hyperfine interaction with the $^{31}P$ nucleus.[813] Both the hyperfine interaction and the low *g*-value are taken to indicate an admixture of higher states. More accurate data have been obtained from molecular beam[943] and spin-exchange optical polarization[944] experiments.

The hyperfine interaction constant is[944] $+55,055,691 \pm 8$ c/s. The *g*-value is[943] $-2{\cdot}00165 \pm 0{\cdot}00039$. The positive sign of the interaction constant has been disputed on theoretical grounds.[945]

### *X*-RAY SPECTRA

The *X*-ray spectra of phosphorus have been reinvestigated by several workers.[75–9, 754–9, 805–7, 815–6] Shifts of the lines as a function of chemical binding have been reported.[754–9, 815] The soft *X*-ray spectrum has also been examined.[80, 815] The $K_{\alpha_1\alpha_2}$ line of phosphorus lies at 6·1549 A., the $K_\beta$ at 5·8038 A., and the $K_\alpha$ absorption edge is at 5·7866 A.[807]

## Diatomic Phosphorus Vapour

The $P_2$ molecule is stable in the vapour only above about 800°C., and has been investigated by spectroscopic means.[66, 81–91, 537, 808–9, 949, 952, 1061] The absorption spectrum has been reported.[950] The equilibrium between diatomic and monoatomic phosphorus has been investigated by mass spectrometry.[951] The bond length in the ground state is 1·894 A., and the vibrational frequency is 780 $\text{cm.}^{-1}$, giving a force constant of 5·56 millidynes/A.[81–2]

## Tetra-atomic Phosphorus Vapour

Electron diffraction experiments[92] have shown that phosphorus vapour consists of symmetrical tetrahedral (point group $T_d$) $P_4$ molecules (Fig. 8). The tetrahedral structure implies interbond angles of 60°, as against the 90° expected for bonds formed from simple *p*-orbitals, and the bonds were regarded as formed from non-cylindrical *spd* hybrid orbitals.[93–5, 818–20] The bond length is 2·21 A.[92] A mass-spectrometer study[96] has confirmed that the sublimation from red phosphorus occurs in tetra-atomic molecules. The existence of $P_8$ molecules has been reported[105] but not confirmed.[96] Later work[946] has been based on the observation[946] of the absorption spectrum of phosphorus vapour in the 3000–1200 A. region. Transitions were observed at 5·1, 5·9, 6·89, 7·7 and 8·4 ev. A theoretical spectrum was calculated[946] on the basis of 3*p* atomic hybridization, and was in reasonable agreement with the experimental data. The calculation indicated strong $\pi$-bonding and delocalization, with a consequent lack of directed valency and elimination of the concept of bent bonds.[946]

## Liquid Phosphorus

The radial distribution curve for liquid phosphorus has been obtained from the *X*-ray diffraction pattern,[104] and the results show that the liquid consists of tetrahedral $P_4$ molecules. The value obtained for the P–P bond length is 2·25 A.

## White Phosphorus

Early work[106–7] on the structure of the cubic high-temperature form has not been confirmed. The latest work[108–9] shows that the cell is body-centred cubic, with $a = 18{\cdot}51$ A., space group probability $I\bar{4}3m$, and that it contains about 56 molecules. The radial distribution curve[108] confirms that tetrahedral $P_4$ molecules are still present. The intensities of the diffracted *X*-ray spots indicate considerable molecular motion, and this is confirmed by the narrow nuclear magnetic resonance line obtained from solid white phosphorus.[110]

The structure of the low-temperature form has not been determined. It is thought to have a low symmetry, probably hexagonal or trigonal, with a large unit cell.[107–8]

The infra-red and Raman spectra of phosphorus as vapour, liquid, solution in carbon disulphide, and as solid white phosphorus have been investigated.[97–103] The results for the different phases are similar and all confirm the presence of tetrahedral

$P_4$ molecules. The active fundamental frequencies, all of which may be described as P–P stretching, are 363 cm.$^{-1}$ ($\nu_2$, $E$, Raman depolarized), 465 cm.$^{-1}$ ($\nu_3$, $F_2$, Raman depolarized, infra-red), and 606 cm.$^{-1}$ ($\nu_1$, $A$, Raman polarized). Valence force constants have been calculated[99, 117, 821]; the value for the P–P stretching force constant in the most general force field, considering increments in the bond lengths as the internal co-ordinates, is 2·065–2·08 millidynes/A.[117, 821] When partial corrections for anharmonicity were made the value was raised to 2·33 millidynes/A.[117]

Nuclear magnetic resonance measurements have been made on phosphorus in carbon disulphide solution and on the liquid, as well as on solid white phosphorus.[110, 171, 637] The chemical shift, relative to 85% orthophosphoric acid, is positive and abnormally large (about +450 p.p.m.). This is attributed to the bent bonds. The shift in carbon disulphide solution is concentration-dependent[637]; this is attributed to interactions with the solvent.

## Red Phosphorus

Five different forms of red phosphorus have been reported,[111] two of which were reported previously.[112] These include triclinic, tetragonal and hexagonal forms, the triclinic form having the highest crystallinity.[111] A report of a cubic form has also appeared.[113] The radial distribution function of amorphous red phosphorus has been determined[104, 114, 953]; the P–P distance is 2·29 A. and the average interbond angle is 99°. The structure of red phosphorus may be regarded as comprising more or less disordered arrays of triply connected phosphorus atoms, the arrays being possibly terminated by impurity groups. The variety in form and properties has been interpreted in terms of different degrees of polymerization and different terminal impurity groups.[115]

In the latest work,[939] only two forms of red phosphorus were reported from preparations between 300° and 610°C. These were forms IV and V (of reference 111), which are reported to be tetragonal (probably) and triclinic respectively. These were characterized by visible fluorescence spectra as well as by $X$-ray diffraction patterns. The other 'forms' reported earlier were claimed to arise from poor crystallinity of forms IV and V.

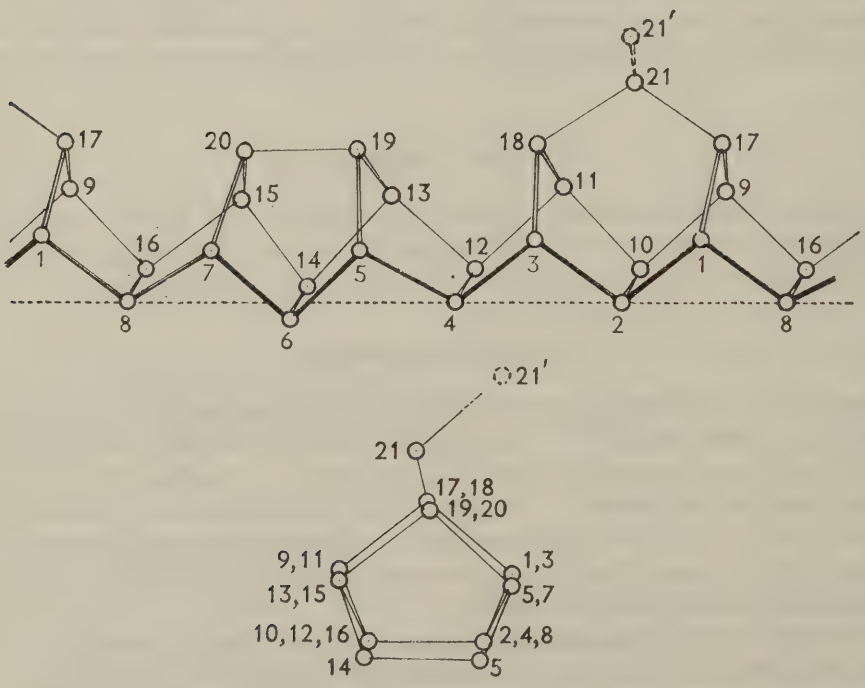

FIG. 1.—Section of a 'tube' of violet phosphorus. Above: parallel perspective. Below: projection parallel to the tube axis (end view)

Recent work[940] on violet (Hittorf) phosphorus, crystallized[941–2] from lead or bismuth at around 500°–600°C., has shown it to be monoclinic, space group $P2/c$, $a = 9{\cdot}21$, $b = 9{\cdot}15$, $c = 22{\cdot}59$ A., $\beta = 106{\cdot}1°$, with 84 atoms per unit cell. The structure is based on $P_8$ and $P_9$ groups linked by two further phosphorus atoms into infinite tube-like structures (Fig. 1). The tubes are packed parallel to each other in layers, successive pairs of layers being approximately perpendicular to each other.

## Black Phosphorus

The results of the first investigation of the structure of black phosphorus[116] are not supported by later work.[114] The structure has recently been refined.[947] The eight-atom cell is orthorhombic, with $a = 3{\cdot}3136$ A., $b = 10{\cdot}478$ A., $c = 4{\cdot}3763$ A., space group *Cmca.* Discrete molecules do not exist, and the atoms (Fig. 2) are in widely separated (5·25 A.) double layers (2·1 A. between layer halves). Each phosphorus atom has two nearest neighbours at 2·224 A. and a third at 2·244 A. The interbond angle in the layers is 96·34°, and the third bond is at 102·09° to the other two.[114] A sample of black phosphorus, showing a different structure, has also been reported, but no details are given.[114] The radial distribution function of amorphous black phosphorus shows a P–P distance of 2·27 A. and an interbond angle of 95·6°.[104]

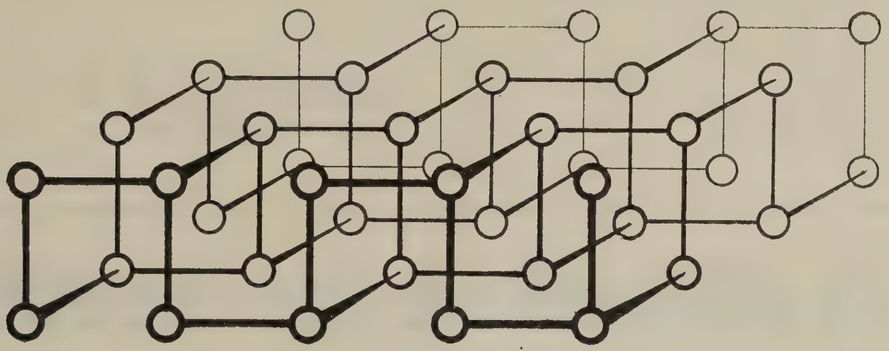

FIG. 2.—The arrangement of atoms in the corrugated planes found in crystalline black phosphorus

## PHOSPHIDES

This class includes the binary and ternary compounds of phosphorus with elements other than hydrogen and the members of Groups VIIA, VIA, and to some extent VA.

The salt-like phosphides, $Li_3P$ and $Na_3P$, are of some interest because of the possibility of a phosphorus negative ion. Unlike the transition metal phosphides, which are of an interstitial character, the alkali metal phosphides have metal–metal distances which are smaller than in the metals, implying covalent or ionic bonding between metal and phosphorus. The structures[1] are of the trisodium arsenide type, in which the phosphorus atom is surrounded by five alkali metal atoms at the corners of a trigonal bipyramid, with geometry very similar to that of the phosphorus pentahalides, suggesting[716] a covalently bonded structure with $sp^3d$ hybridization. There is therefore little evidence for a phosphorus negative ion in these compounds.

The alkaline-earth phosphides of known structure[7,8] have the phosphorus atom surrounded by six metal atoms at the corners of a tetragonal bipyramid. There are two types of phosphorus site, one in the centre of the bipyramid, and one displaced from the centre. All the phosphides of Group IIIA elements of which the structures have been investigated have the zinc blende three-dimensional polymer type of structure, with fourfold tetrahedral co-ordination of both the elements, indicating $sp^3$ hybridization. The monophosphides are isoelectronic with the elements of Group

Table II.—Structural Data on Phosphides

| Compound | Crystal system | Space group | Structure prototype | Unit cell data | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | a<br>A. | b<br>A. | c<br>A. | Z | |
| $AgP_2$ | Monoclinic | $P2_1/c$ | $CuP_2$ | 6·218 | 5·056<br>$\beta = 113{\cdot}48°$ | 7·804 | | 969 |
| $AgGe_2P_3$ | Orthorhombic | | | 10·3 | 14·6 | 8·9 | | 970 |
| AlP | Cubic | $F\bar{4}3m$ | Zinc blende | 5·451 | | | 4 | 43 |
| | | | | 5·467 | | | | 968 |
| $B_{13}P_2$ | Trigonal | $R\bar{3}m$ | — | 5·984 | | 11·85 | 1 | 42, 1003 |
| BP | Cubic | $F\bar{4}3m$ | Zinc blende | 4·538 | | | 4 | 41 |
| $Be_3P_2$ | Cubic | $Ia3$ | $Tl_2O_3$ | 10·15 | | | 16 | 8 |
| $Ca_3P_2$ | Tetragonal | — | — | 5·44 | | 6·59 | — | 231 |
| CaP | Tetragonal | — | — | 5·93 | | 7·94 | — | 231 |
| $Cd_3P_2$ | Tetragonal | $P4_2/nmc$ | — | $8{\cdot}74_6$ | | 12·28 | 8 | 13 |
| $CdP_2$ | Tetragonal | $P4_12_12$ or $P4_32_12$ | — | 5·28 | | 19·70 | 8 | 13 |
| $CdP_4$ | Monoclinic | $P2_1/c$ | — | 5·26 | 5·18<br>$\beta = 80°32'$ | 7·64 | 2 | 14 |
| $CdSiP_2$ | Tetragonal | $I\bar{4}2d$ | Chalcopyrite | 5·678 | | 10·431 | | 975 |
| CeP | Cubic | $Fm3m$ | NaCl | $6{\cdot}01_3$ | | | 4 | 16 |
| $Co_2P$ | Orthorhombic | $Pbnm$ | $PbCl_2$ | 6·65 | 5·71 | 3·52 | 4 | 35 |
| | | | | 6·608 | 5·644 | 3·512 | | 651 |
| CoP | Orthorhombic | $Pbnm$ | MnP | 5·588 | 5·066 | 3·274 | 4 | 11, 27–8, 35 |
| | | | | 5·587 | 5·077 | 3·281 | | 847 |
| $CoP_3$ | Cubic | $Im3$ | Skutterudite, $CoAs_3$ | 7·706 | | | 8 | 652 |
| $CoP_{0{\cdot}6}B_{0{\cdot}1}$ | Orthorhombic | $Pbnm$ | MnP | 5·623 | 5·050 | 3·277 | 4 | 847 |
| CoPS | Cubic | | Cobaltite | 5·422 | | | | 957 |
| $CoPS_3$ | Trigonal | | | 5·91 | 19·1 | | 6 | 1119 |
| $CoP_{0{\cdot}6}Si_{0{\cdot}4}$ | Orthorhombic | $Pbnm$ | MnP | 5·653 | 5·060 | 3·264 | 4 | 847 |
| $Cr_3P$ | Tetragonal | $I\bar{4}$ | $Fe_3P$ | 9·144 | | 4·567 | 8 | 30, 37 |
| CrP | Orthorhombic | $Pbnm$ | MnP | 6·108 | 5·362 | 3·113 | 4 | 37, 47, 847 |
| $(Cr_{1/4}Fe_{3/4})_3P$ | Tetragonal | $I\bar{4}$ | $Fe_3P$ | 9·080 | | 4·496 | 8 | 30 |
| $Cu_3P$ | Hexagonal | $P\bar{3}c1$ | — | 6·942 | | 7·098 | 6 | 10, 12$^{(b)}$ |
| $CuP_2$ | Monoclinic | $P2_1/c$ | $AgP_2$ | 5·802 | 4·807<br>$\beta = 112{\cdot}68°$ | 7·525 | | 969 |
| CuPS | Cubic | | CuBS | 9·70 | | | | 1173 |
| $CuPS_2$ | Hexagonal | | Wurtzite, ZnS superstructure | 3·652 | | 6·085 | | 1323 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| CuPSe | Cubic | | CuBS | 10·15 | | | | 1173 |
| $CuPSe_2$ | Hexagonal | | Wurtzite, ZnS superstructure | 3·853 | | 6·392 | | 1323 |
| $Fe_3P$ | Tetragonal | $I\bar{4}$ | — | 9·090 | | 4·446 | 8 | 26, 29–30, 652 |
| $Fe_2P$ | Hexagonal | $P321$ | — | 5·852 | | 3·453 | 3 | 24–6 |
| | | $P\bar{6}2m$ | | 5·865 | | 3·456 | 3 | 651 |
| FeP | Orthorhombic | $Pbnm$ | MnP | $\{$5·782 | 5·177 | 3·089 | 4 | 11, 27 |
| | | | | 5·792 | 5·191 | 3·099 | | 847 |
| $FeP_2$ | Orthorhombic | $Pnnm$ | Marcasite, $FeS_2$ | $2{\cdot}72_5$ | $4{\cdot}97_5$ | $5{\cdot}65_7$ | 2 | 22, 23 |
| $FePS_3$ | Trigonal | | | 5·95 | 19·2 | | 6 | 1119 |
| $FePSe_3$ | Trigonal | | | 6·28 | 19·8 | | 6 | 1119 |
| $FeP_{0\cdot5}Si_{0\cdot5}$ | Orthorhombic | $Pbnm$ | MnP | 5·853 | 5·242 | 3·059 | 4 | 847 |
| GaP | Cubic | $F\bar{4}3m$ | Zinc blende | 5·450 | | | 4 | 43, 44 |
| $HfP_2$ | Orthorhombic | | | 6·467 | 8·646 | 3·497 | | 954 |
| $Hg_3P_2I_2$ | Monoclinic | $P2_1/c$ | — | 13·07 | 12·44<br>$\beta = 120°\ 12'$ | 17·16 | 12 | 646 |
| InP | Cubic | $F\bar{4}3m$ | Zinc blende | 5·451 | | | 4 | 43, 45 |
| $Ir_2P$ | Cubic | $Pm3m$ | $CaF_2$ | 5·543 | | | 4 | 39, 48 |
| $IrP_3$ | Cubic | $Im3$ | Skutterudite, $CoAs_3$ | 8·015 | | | 4 | 48 |
| IrPS | Cubic | | Cobaltite | 5·650 | | | | 957 |
| IrPSe | Cubic | | Pyrite, $FeS_2$ superstructure | 5·798 | | | | 957 |
| $KPH_2$ | Monoclinic | $C2/m$ | — | 7·952 | 4·450<br>$\beta = 120{\cdot}5°$ | 5·275 | 2 | 846 |
| LaP | Cubic | $Fm3m$ | NaCl | $6{\cdot}01_3$ | | | 4 | 16 |
| $Li_3P$ | Hexagonal | $P6_3/mmc$ | $Na_3As$ | 4·980 | | 8·797 | 2 | 1 |
| $Li_3AlP_2$ | Orthorhombic | $Ibca$ | $CaF_2$ rhombically deformed | 11·47 | 11·61 | 11·73 | 16 | 6 |
| $Li_3GaP_2$ | Cubic | $Pm3m$ | $CaF_2$ superlattice | 11·74 | | | 16 | 3 |
| $Li_5GeP_3$ | Cubic | $Pm3m$ | $CaF_2^{(a)}$ | 5·88 | | | 4/3 | 3 |
| LiMgP | Cubic | $Pm3m$ | $CaF_2^{(a)}$ | 6·01 | | | 4 | 2 |
| $Li_5SiP_3$ | Cubic | $Pm3m$ | $CaF_2^{(a)}$ | 5·84 | | | 4/3 | 3 |
| $Li_5TiP_3$ | Cubic | $Pm3m$ | $CaF_2^{(a)}$ | 5·95 | | | 4/3 | 3 |

*Table II.—(continued)*

| Compound | Crystal system | Space group | Structure prototype | Unit cell data |  |  |  | References |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | *a*<br>A. | *b*<br>A. | *c*<br>A. | *Z* |  |
| $Li_7VP_4$ | Cubic | *Pm3m* | $CaF_2^{(a)}$ | $5{\cdot}97_5$ |  |  | 1 | 4 |
| LiZnP | Cubic | *Pm3m* | $CaF_2^{(a)}$ | $5{\cdot}76_8$ |  |  | 4 | 2 |
| $LiPN_2$ | Tetragonal | — | — | 4·566 |  | 7·145 | — | 5 |
| LuP | Cubic |  |  | 5·535 |  |  |  | 992, 993 |
| $Mg_3P_2$ | Cubic | *Ia*3 | $Tl_2O_3$ | 10·15 |  |  | 16 | 7, 8, 9 |
| $Mn_3P$ | Tetragonal | $I\bar{4}$ | $Fe_3P$ | 9·181 |  | 4·568 | 8 | 30, 1001 |
| $Mn_2P$ | Hexagonal | $P\bar{6}2m$ | $Fe_2P$ | 6·081 |  | 3·460 | 3 | 27, 36, 651, 1001 |
| MnP | Orthorhombic | *Pbnm* | NiAs (distorted) | {5·905 | 5·249 | 3·167 | 4 | 11, 27–8, 34, 36, 847 |
|  |  |  |  | 5·918 | 5·258 | 3·172 |  |  |
| $(Mn_{1/4}Fe_{3/4})_3P$ | Tetragonal | $I\bar{4}$ | $Fe_3P$ | 9·095 |  | 4·477 | 8 | 30 |
| $Mo_3P$ | Tetragonal | $I\bar{4}$ | $Fe_3P$ (or $\alpha$-$V_3S$) | 9·729 |  | 4·923 | 8 | 37 |
|  |  |  |  |  |  |  |  | 956 |
|  |  | $I\bar{4}2m$ |  | 9·794 |  | 4·827 |  | 986 |
| $Mo_4P_3$ | Orthorhombic | *Pnma* |  | 12·428 | 3·158 | 20·440 |  | 987 |
| MoP | Hexagonal | $P\bar{6}m2$ | WC | 3·23 |  | 3·20 | 1 | 37 |
| $Na_3P$ | Hexagonal | $P6_3/mmc$ | $Na_3As$ | 4·980 |  | 8·797 | 2 | 1 |
| $Nb_7P_4$ | Monoclinic |  |  | 14·950 | 3·440<br>$\beta$=104·74° | 13·848 |  | 984 |
| $\alpha$-$NbP_{0{\cdot}95}$ | Tetragonal | *F*4/*mmm* | — | 3·32 |  | 5·69 | 4 | 37, 961, 962 |
| $\beta$-NbP | Tetragonal | $I4_12$ | NbAs | 3·33 |  | 11·37 | 8 | 37, 961, 964 |
| $NbP_2$ | Monoclinic |  |  | 8·8715 | 3·2663<br>$\beta$=119·007° | 7·5194 |  | 985 |
| NdP | Cubic | *Fm*3*m* | NaCl | $5{\cdot}82_6$ |  |  | 4 | 16 |
| $Ni_3P$ | Tetragonal | $I\bar{4}$ | $Fe_3P$ | 8·952 |  | 4·388 | 8 | 30–33, 844 |
|  |  |  |  | 8·954 |  | 4·387 |  | 652 |
|  |  |  |  | 8·954 |  | 4·386 |  | 1002 |
| $Ni_5P_2$ | {Hexagonal |  |  | 13·220 |  | 24·632 |  | 980 |
|  | Trigonal |  |  | 6·608 |  | 24·634 |  | 981 |
| $Ni_{12}P_5$ | Tetragonal | *I*4/*m* | — | 8·646 |  | 5·070 | 2 | 652 |
| {$Ni_7P_3$ | Cubic | — | — | 8·63 |  |  | 6 | 32 |
| $Ni_{2{\cdot}4}P$ | Tetragonal | — | — | 8·646 |  | 5·070 |  | 652 |
| $Ni_2P$ | Hexagonal | *P*321 | — | $5{\cdot}85_0$ |  | 3·365 | 3 | 32 |
|  |  |  |  | 5·864 |  | 3·385 |  | 651–2 |
|  |  |  |  | 5·859 |  | 3·382 |  | 1001 |

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| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $Ni_5P_4$ | Hexagonal | | | 6·789 | | 10·986 | | 981, 982 |
| $NiP_3$ | Cubic | *Im*3 | Skutterudite, $CoAs_3$ | 7·819 | | | 4 | 652 |
| NiPS | Cubic | | Cobaltite | 5·544 | | | | 957 |
| $NiPS_3$ | Trigonal | | | 5·83 | 19·0 | | 6 | 1119 |
| $NiPSe_3$ | Trigonal | | | 6·15 | 19·6 | | 6 | 1119 |
| $OsP_2$ | Orthorhombic | *Pnnm* | Marcasite, $FeS_2$ | 5·098 | 5·898 | 2·918 | 2 | 48 |
| $Pd_{4\cdot8}P$ | Monoclinic | $P2_1$ | | 5·004 | 7·606<br>$\beta = 95{\cdot}63°$ | 8·416 | | 989 |
| $Pd_3P$ | Orthorhombic | *Pbnm* | Cementite, $FeC_3$ | 5·166 | 5·971 | 7·445 | 4 | 845, 959 |
| $Pd_5P_2$[958] (or $Pd_7P_3$)[959] | Rhombohedral | | — | 7·28 | $\alpha = 110{\cdot}12°$ | | | 959 |
| | | | | (high temp. form) | | | | |
| $Pd_{0\cdot75-1\cdot0}P$ | Orthorhombic | *Pnma* | — | 5·980<br>−5·645 | 7·440<br>−7·558 | 5·164<br>−5·071 | 4 | 338 |
| $PdP_2$ | Monoclinic | *I*2/*a* | — | 6·207 | 5·857<br>$\beta = 111{\cdot}80°$ | 5·874 | 4 | 959, 999 |
| | | | | 6·777 | 5·856<br>$\beta = 126{\cdot}42°$ | 6·206 | | 960 |
| $PdP_3$ | Cubic | *Im*3 | Skutterudite, $CoAs_3$ | 7·705 | | | 8 | 48 |
| PrP | Cubic | *Fm*3*m* | NaCl | $5{\cdot}86_0$ | | | 4 | 16 |
| $PtP_2$ | Cubic | *Pa*3 | Pyrite, $FeS_2$ | 5·6956 | | | 4 | 38, 48, 991, 984 |
| PuP | Cubic | *Fm*3*m* | NaCl | 5·644 | | | 4 | 20, 997, 998 |
| $RbPH_2$ | Monoclinic | *C*2/*m* | — | 8·419 | 4·746<br>$\beta = 122{\cdot}0°$ | 5·513 | 2 | 846 |
| $Rh_2P$ | Cubic | *Pm*3*m* | $CaF_2$ | 5·498 | | | 4 | 39, 48, 959 |
| $Rh_4P_3$ | Orthorhombic | *Pnma* | | 11·662 | 3·317 | 9·994 | 4 | 40 |
| $RhP_3$ | Cubic | *Im*3 | Skutterudite, $CoAs_3$ | 7·996 | | | 8 | 48 |
| RhPS | Cubic | | Cobaltite | 5·640 | | | | 957 |
| RhPSe | Cubic | | Cobaltite | 5·795 | | | | 957 |
| $Ru_2P$ | Orthorhombic | *Pbnm* | $PbCl_2$ | 5·902 | 3·859 | 6·896 | 4 | 48 |
| RuP | Orthorhombic | *Pbnm* | MnP | 5·520 | 3·168 | 6·120 | 4 | 11, 48, 847 |
| $RuP_2$ | Orthorhombic | *Pnnm* | Marcasite, $FeS_2$ | 5·115 | 5·888 | 2·870 | 2 | 48 |
| RuPS | Monoclinic | | Arsenopyrite | 5·77 | 5·77<br>$\beta = 111{\cdot}2°$ | 5·81 | | 988 |
| RuPSe | Monoclinic | | Arsenopyrite | 5·97 | 5·92<br>$\beta = 111{\cdot}8°$ | 5·98 | | 988 |
| ScP | Cubic | *Fm*3*m* | NaCl | 5·312 | | | | 965 |
| | | | | 5·302 | | | 4 | 1393 |
| SmP | Cubic | *Fm*3*m* | NaCl | 5·760 | | | 4 | 17 |
| SnP | Hexagonal | *P*321, *P*3*m*1, or $P\bar{3}m1$ | | 8·78 | | 5·98 | 8 | 46 |

Table II.—(continued)

| Compound | Crystal system | Space group | Structure prototype | Unit cell data | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | a A. | b A. | c A. | Z | |
| $Ta_3P$ | Tetragonal | | $Ti_3P$ | 10·154 | | 5·012 | | 990, 985 |
| $Ta_2P$ | Orthorhombic | | | 14·419 | 11·552 | 3·399 | | 985 |
| $Ta_5P_4$ | Orthorhombic | | | 14·420 | 11·547 | 3·400 | | 990, 985 |
| α-TaP | Tetragonal | *F4/mmm* | α-NbP | 3·320 | | 5·69 | 4 | 37 |
| β-TaP | Tetragonal | *I4₁2* | β-NbP | 3·334 | | 11·377 | 8 | 37, 985 |
| $TaP_2$ | Monoclinic | | | 8·8608 | 3·2677<br>β-119·308° | 7·4882 | | 985 |
| $ThP_{0\cdot55-0\cdot96}$ | Cubic | | | 5·830–5·840 | | | | 994–996 |
| $Th_3P_4$ | Cubic | *I4̄3d* | — | 8·600 | | | 4 | 21 |
| $Ti_3P$ | Tetragonal | | $V_3P$ | 9·956 | | 4·988 | | 966, 977 |
| $Ti_2P$ | Hexagonal | | $Fe_2P$ | 6·71 | | 3·46 | | 977 |
| $Ti_3P_2$ | Tetragonal | | | 7·48 | | 10·49 | | 977 |
| $Ti_5P_3$ ($TiP_{\sim0\cdot6}$) | Hexagonal | *P6₃/mcm* | $Mn_5Si_3$ | 7·238 | | 5·088 | | 978–9 |
| $Ti_4P_3$ | Cubic | | | 7·425 | | | | 977 |
| TiP | Hexagonal | *P6₃/mmc* | — | 3·487 | | 11·65 | 4 | 37 |
| $TiP_2$ | Orthorhombic | | | 6·181 | 8·256 | 3·346 | | 954 |
| $Ti_3PO_2$ | Hexagonal (pseudocubic) | *P3̄m1* | — | 4·415 | | | — | 840 |
| TmP | Cubic | | | 5·573 | | | | 992–3 |
| UP | Cubic | *Fm3m* | NaCl | 5·589 | | | 4 | 19, 1012 |
| $U_3P_4$ | Cubic | *I4̄3d* | $Th_3P_4$ | $8\cdot19_7$ | | | 4 | 19, 1315 |
| $UP_2$ | Tetragonal | *P4/nmm* | — | 3·800 | | 7·762 | 2 | 18 |
| $V_3P$ | Tetragonal | | $Ti_3P$ | 9·387 | | 4·756 | | 966 |
| VP | Hexagonal | *P6₃/mmc* | NiAs | 3·18 | | 6·22 | 2 | 37 |
| $W_2P$ | Hexagonal | — | — | 6·18 | | 6·78 | — | 339 |
| WP | Orthorhombic | *Pbnm* | MnP | 6·219 | 3·238 | 5·717 | 4 | 37 |
| | | | | 6·222 | 3·249 | 5·734 | | 847 |
| α-$WP_2$ | Monoclinic | | $NbAs_2$ | 8·5022 | 3·1695<br>β=119·367° | 7·4660 | | 954–5 |
| β-$WP_2$ | Orthorhombic | | $MoP_2$ | 3·166 | 11·161 | 4·973 | | 955–6 |
| YP | Cubic | *Fm3m* | NaCl | 5·661 | | | | 961–2 |
| $Zn_3P_2$ | Tetragonal | *P4₂/nmc* | — | $8\cdot09_7$ | | 11·45 | 8 | 13 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $ZnP_2$ | Tetragonal | $P4_12_12$ or $P4_32_12$ | — | 5·07 | | 18·65 | 8 | 13, 972 |
| | Monoclinic | | | 8·85 | 7·29<br>$\beta = 102{\cdot}3°$ | 7·56 | | 967 |
| $ZnGeP_2$ | Tetragonal | $I\bar{4}2d$ | Chalcopyrite, $CuFeS_2$ | 5·46 | | 10·74 | 4 | 15, 973–5 |
| $Zn_3PI_3$ | Cubic | $F\bar{4}3m$ | (Zinc blende defect and disordered) | $5{\cdot}94_5$ | | | | 1172 |
| $ZnSiP_2$ | Tetragonal | $I\bar{4}2d$ | Chalcopyrite, $CuFeS_2$ | 5·398 | | 10·440 | | 973–5 |
| $\alpha$-$ZrP_{0{\cdot}9}$ | Cubic | $Fm3m$ | NaCl | 5·242 | | | 4 | 37, 963 |
| $\beta$-ZrP | Hexagonal | $P6_3/mmc$ | TiP | 3·684 | | 12·554 | 4 | 37, 963 |
| $ZrP_2$ | Orthorhombic | | | 6·494 | 8·744 | 3·513 | | 954 |
| ZCoP | Orthorhombic | | | 6·332 | 3·698 | 7·160 | | 983 |
| ZrFeP | Orthorhombic | $Pnma$ | | 6·309 | 3·740 | 7·172 | | 983 |
| $Zr_3PO_2$ | Hexagonal (pseudo-cubic) | $P\bar{3}m1$ | — | 4·779 | | | — | 840 |

(a) P on Ca sites; other atoms statistically distributed on F sites.
(b) Doubt has been cast on this structure.[154]

IVA, and those of aluminium, gallium and indium are semiconductors. The phosphides of the transition, rare earth and actinide metals are generally of an interstitial character. Most of the compounds show the typical expansion of the metal–metal interatomic distance relative to the pure metal. Zirconium, niobium and tantalum phosphides each occur in two forms, of which the α-phases are deficient in phosphorus, corresponding approximately to $MP_{0\cdot9}$.

The $^{57}$Fe Mössbauer spectra of three iron phosphides and the $^{31}$P NMR spectrum of FeP have been examined.[1062] FeP showed an isomer shift of 0·25 mm./sec. with respect to natural iron, a quadrupole splitting of 0·65 mm./sec., and an NMR chemical shift of $-375$ p.p.m. with respect to orthophosphoric acid. $Fe_2P$ at room temperature showed a singlet and a doublet, of equal intensity, unresolved, with isomer shifts of 0·16 (singlet) and 0·58 mm./sec. (doublet) and a doublet quadrupole splitting of 0·40 mm./sec. At liquid air temperatures, below the Curie point, it gave a complex superposition of two six-line patterns, one from each type of site. $Fe_3P$ gave a complex 18-line pattern, with six lines from each of three sites.[1062]

The infra-red spectra of the semiconducting phosphides have received attention from the point of view of determining the energy gap. The infra-red absorption and reflection,[49,50] Raman spectrum[976] and lattice vibrations of gallium phosphide, and the infra-red absorption of indium phosphide[51] have been investigated. The visible absorption spectrum of gallium phosphide at liquid nitrogen temperatures has been investigated.[1000]

Gallium phosphide and trizinc diphosphide have also been investigated by nuclear magnetic resonance.[830–1,971] The observed line widths of the $^{69}$Ga, $^{71}$Ga and $^{31}$P resonances (2·26, 2·26 and 2·9 gauss respectively) could not be accounted for by dipolar broadening alone; the additional broadening was thought to be due to indirect nuclear exchange interactions. In $Zn_3P_2$ the $^{31}$P NMR spectrum[971] showed two peaks of equal intensity, with chemical shifts $+217$ and $+250$ p.p.m. relative to 85% $H_3PO_4$, in accordance with the crystal structure.[13]

The series of transition-metal monophosphides of vanadium, chromium, iron, cobalt and manganese have been investigated by NMR[1117–8] and the results related to magnetic susceptibility measurements and to the electronic band structures. Resonance shifts of the $^{31}$P resonance, relative to that in red phosphorus, of 0·023, $-0·17$, 0·034, 0·36% were observed in VP, CrP, FeP, CoP respectively at room temperature.[1117] The $^{59}$Co resonance shift, relative to potassium hexacyanocobaltate, in CoP was $-0·36$% at 4·2 and 2°K.[1117]

The available structural data on phosphides are summarized in Table II.

## DIATOMIC AND TRIATOMIC MOLECULES CONTAINING PHOSPHORUS

All these molecules are unstable at room temperature and have been investigated only by spectroscopic means.

PN has been investigated by several workers[66,118–23,952,1044]; the bond length is 1·491 A.,[118,122] and the vibrational frequency 1337 cm.$^{-1}$, giving a force constant of 10·1 millidynes/A.[122] The bands arise from $'\pi \rightarrow {}'\Sigma$ transitions.

PO has a bond length of 1·45 A.[124–5]; the vibrational frequency is 1231 cm.$^{-1}$ and the force constant 9·4 millidynes/A.[124] The spectrum has also been investigated by several other workers.[91,118,125–31,311,541,810,1034–9,1043–4,1060,1146–9] There has been disagreement over the value of the dissociation energy.[91,125,1034–5] The latest work[1035] favours a value of 5·4 ev. The observed ultra-violet bands have been assigned to $^2\Sigma \rightarrow {}^2\pi$ and $^2\pi$–$^2\pi$ (ground state) transitions.

The PH molecule[132–5,533] has a bond length of 1·43 A. and a vibrational frequency of 2380 cm.$^{-1}$ giving a force constant of 3·25 millidynes/A.,[135] corresponding to a single bond. A complex band system was assigned to a $^3\pi_1 - {}^3\Sigma$ transition.

The molecule PC has been reported[136] as having a bond length of 1·5622 A.

The molecules PCl, PBr[137], PI[137–8], PS, PS$^+$ and PO$^+$ [90–1] have also been reported.

The relation of such molecules to other diatomic molecules has received considerable attention in discussions[139-43] of the regularities in the vibration spectra of diatomic molecules. The diatomic hydrides and PH have received particular attention.[144-6] The vibration frequencies of the molecule FPF have been stated[1161] to be 890, 775 and 376 cm.$^{-1}$, and mean amplitudes of vibration have been calculated.[1162]

The emission spectra of the molecules HPO and DPO have been reported.[1033, 1041-2]

## PHOSPHINE

Solid phosphine shows a phase transition at 88·5°K.[167]; at 103°K. it has a cubic crystal structure[147] with a four-molecule cell of side $a = 6{\cdot}31$ A. and space group *Fd*3 or *Pn*3*m*. The phosphorus atoms are stated to lie on a face-centred cubic lattice, but the data are also reported to be equally compatible with the ammonia structure.[154] The positions of the hydrogen atoms were not determined. The molecular dimensions of phosphine have been determined from the microwave rotational spectra of phosphine and deuterated phosphines,[148-9, 488, 1008-9] from the Coriolis coupling in the vibration–rotation spectra,[150, 156, 491] and from electron diffraction experiments.[340] The P–H bond length is 1·419 A., a value in agreement with a prediction[499] based on Badger's rule, and the H–P–H angle lies between 93° 20′ and 93° 50′. The intermixture of $sp^3$ hybridization with the $p^3$ is therefore small. The dipole moment is 0·58 Debye units.[149, 1008] Several authors have discussed the electronic structure[501-5, 1019, 1032] and the dipole moment[504, 506, 1019] from a theoretical viewpoint. The interbond angle has also been calculated theoretically, and a value in reasonable agreement with the experimental value obtained.[507-9]

The ultra-violet spectrum of phosphine has been examined[151-2, 163, 1006-7, 1017-8] in connection with its photochemical decomposition. The band structure of phosphine and deuterophosphine in the 1850–2500 A. region has been explained on the assumption that the upper state of $PH_3$ and $PD_3$ is pyramidal, with a barrier to inversion so low that all observed transitions are to levels above the barrier.[163, 1006-7] The Verdet constant of phosphine at 0°C., 760 mm. and 5780 A. is $57 \times 10^{-6}$.[500] The infra-red[150, 153, 156-63, 166, 173, 489, 491, 493, 496-7] and Raman[164-5, 494-5] spectra of phosphine and the deuterophosphines[153, 173, 493-5] have been investigated. The P–H stretching vibrations, $\nu_1(A)$ at 2323 cm.$^{-1}$ and $\nu_3(E)$ at 2328 cm.$^{-1}$ [491] are resolved with difficulty. The symmetrical and degenerate deformation vibrations, $\nu_2$ and $\nu_4$, occur at 990 and 1121 cm.$^{-1}$ respectively. In trideuterophosphine the P–D stretching vibrations appear at 1694 cm.$^{-1}$, and $\nu_2$ and $\nu_4$ at 730 and 806 cm.$^{-1}$ respectively.[153] The infra-red spectra of the two phases of solid phosphine and trideuterophosphine have been determined.[167, 1021] The force field of phosphine has been worked out by several authors[168, 1023-5, 1012] by considering the spectra of phosphine, deuterated and tritiated phosphines, anharmonicities, rotation distortion constants and Coriolis coupling constants.[1024-5, 1012] The valence stretching force constant is 3·328 millidynes/A.[168] 3·3326,[1024] 3·10,[1025] 3·1222.[1012] Earlier treatments of the force field[163, 169, 492, 498, 827] involved various assumptions. The absolute intensities of the fundamental infra-red bands of phosphine have been determined[163] and an attempt was made to determine the bond dipole moments. The results are not entirely self-consistent; it appears that the vibrational bond moments could not be identified with the static ones. The mean amplitudes of vibration of phosphine have been calculated.[1026] The potential barrier to inversion in phosphine has been calculated approximately as 17·1 kcal./mole[490, 498] and racemization rate has been calculated.[155] The vibrational relaxation has been investigated[1022] and overall relaxation times of 1·96 and $3{\cdot}43 \times 10^{-7}$ sec. obtained for $PH_3$ and $PD_3$ respectively.[1022]

The phosphorus nuclear magnetic resonance spectrum of liquid phosphine at −90°C. has been determined.[110, 171, 225] The chemical shift is positive and large (+238 p.p.m.). This is correlated[171] with the nearly pure $p^3$ hybridization. The phosphorus–proton spin-spin coupling is 179 c/s.[225] The proton NMR spectrum of phosphine has been investigated in a variety of solvents.[1063] Both the chemical shift and the coupling constant show considerable solvent and temperature dependence, ranges of 8·10–8·45 $\tau$ and 183–190 c/s being observed.[1063]

The mass spectrum of phosphine has been investigated.[1027–9] The ionization potential is 10·02 ± 0·05 ev.[1029]

The $PH_2$ radical has been observed in the ESR spectrum of $\gamma$-irradiated phosphine in a krypton matrix at 4·2°K.[1013] The *g*-value is 2·0087. The electronic structure of the radicals PH and $PH_2$ has been treated theoretically[1014] with results in reasonable agreement with the experimental data[1015–6, 1020] obtained from observations of the flash photolysis of phosphine.

## Phosphine Derivatives

Biphosphine, $H_2PPH_2$, has been investigated independently by infra-red spectroscopy (vapour and solid) and *X*-ray powder photography[174] and by Raman spectroscopy of the liquid.[641–2] The characters of the bands in the vapour-phase infra-red spectrum suggest a gauche configuration of the $PH_2$ groups, with $C_2$ molecular symmetry. A similar suggestion was based on the number of lines in the Raman spectrum.[641] Values of 2·99 and 1·85 millidynes/A. for the P–P and P–H stretching force constants respectively were obtained from the totally symmetric vibrations. Eight of the nine lines expected for $C_2$ symmetry were observed but two of these, at 412 and 456 cm.$^{-1}$, are difficult to assign satisfactorily, and later work[642] on the Raman spectrum of the deuterated compound suggests that these lines may arise from higher phosphorus compounds. The deduction of $C_2$ symmetry for biphosphine cannot therefore be regarded as conclusive.

The compounds $H_2PSH$ and $D_2PSD$, identified by their mass spectra, show a sharp infra-red absorption at 477 cm.$^{-1}$ assigned to the P–S single bond.[1005]

The *X*-ray data suggest a monoclinic two-molecule cell with $a = 3{\cdot}6$ A., $b = 6{\cdot}6$ A., $c = 3{\cdot}2$ A., $\beta = 104°$, space group *Pm* or $P_2$.[174] These deductions are again not regarded as conclusive. The NMR spectrum[1010] of diphosphine is consistent with rapid interconversion between two skew forms of the molecule. The PH spin-spin coupling constant is close to that in phosphine, suggesting similar bond lengths and hybridizations between the two molecules.

The spectra of a number of silicon- and germanium-substituted phosphines have been studied.[1004, 1030–1, 1040] Trisilylphosphine, $(SiH_3)_3P$, is deduced to have a planar or near-planar skeleton, from the non-appearance in the infra-red of the breathing frequency which gives a strong polarized Raman band at 414 cm.$^{-1}$[1030] The asymmetric P–$Si_3$ stretch is at 455 cm.$^{-1}$[1030] In the infra-red spectrum[1031] of disilylphosphine, $(SiH_3)_2PH$, the following assignments were made[1031]: PH 2300 cm.$^{-1}$, SiH 2150, $SiH_3$ asym. deformation 942/932. $SiH_3$ sym. deformation 888/878. In disilanylphosphine, $Si_2H_5PH_2$, infra-red assignments were as follows[1031]: 736–724 cm.$^{-1}$ $SiH_3$ wag, 1073 $PH_2$ deformation, 784 $PH_2$ wag, 637/628 $PH_2$ twist, 515–475 (weak) SiP stretch. The infra-red spectrum of monosilylphosphine, $H_3SiPH_2$, has been reported and a vibrational assignment made.[179] The P–H stretching vibrations absorb at 2312 cm.$^{-1}$, the $PH_2$ deformation at 1068·5 cm.$^{-1}$, and the Si–P stretching at 454 cm.$^{-1}$. NMR data on these compounds[1031, 1040] are as follows: $H_3SiP$, 6·3$\tau$; $((H_3Si)_2PH)$, 6·27$\tau$; $(H_3SiPH_2)$ (HP), 9·60$\tau$; $H_3SiSi(P)$, 6·81$\tau$; $SiSiH_2P$, 6·43$\tau$; $H_2P$, 8·75$\tau$ $(Si_2H_5PH_2)$, 8·69$\tau$ $(SiH_3PH_2)$. $J_{\mathrm{PH}}$ 184·0 c/s, $J_{\mathrm{HP(Si}H_3)_2}$ 17·5 c/s, $J_{\mathrm{H_2PSi}H3}$ 16·2 c/s, $J_{\mathrm{Si_2H_5}PH_2}$ 182·5 c/s, $J_{\mathrm{SiH_3}PH_2}$ 180 c/s, $J_{\mathrm{Si}H_2\mathrm{PH_2}}$ 18·5 c/s, $J_{\mathrm{H_2}P\mathrm{SiH_2Si}H_3}$ 2·0 c/s, $J_{H_2\mathrm{PSi}H_2-}$ 5·8 c/s, $J_{\mathrm{P-Si}H_2\mathrm{Si}H_3}$ 3·0 c/s, $J_{(\mathrm{Si}H_3)_2\mathrm{P}H}$ 5·1 c/s, $J_{\mathrm{Si}H_3\mathrm{PH_2}}$ 204 c/s.

Trigermylphosphine, $(GeH_3)_3P$, has been studied by infra-red and Raman spectra, which suggest a non-planar skeleton.[1004] NMR data on germylphosphine, $GeH_3PH_2$, are as follows: $PH_2$ 8·39$\tau$, $GeH_3$ 6·33$\tau$, $J_{\mathrm{HH}}$ 4·8 c/s, $J_{\mathrm{PH_2}}$ 180 c/s, $J_{P\mathrm{Ge}H_3}$ 15·3 c/s.[1040]

The crystal structure of phosphonium iodide, $PH_4I$, has been investigated.[175] The structure is a distortion of the cæsium chloride arrangement, with a two-molecule tetragonal unit cell of dimensions $a = 6{\cdot}34$ A., $b = 4{\cdot}62$ A., with space group *P*4/*nmm*, and it is similar to the low-temperature phase III ammonium bromide and ammonium iodide structures.[177, 312] The infra-red spectrum has been investigated[177, 259] over a wide range of temperatures[177] and the Raman spectrum has also been reported[176,1011]; all the spectra are consistent with the room temperature crystal structure.[177] The strong bands in the infra-red spectrum, at 932–54 and 2372 cm.$^{-1}$, are derived from the triply degenerate bending and stretching modes respectively of an isolated $PH_4^+$ ion. The symmetrical breathing mode appears in the Raman spectrum at 2304 cm.$^{-1}$ The infra-red spectrum of the deuterated derivative was also investigated[177]; the strong bands are at 683–701 and 1740 cm.$^{-1}$ The proton nuclear magnetic resonance spectra of crystalline phosphonium iodide and phosphonium bromide have been examined[178] and used to deduce a value for the P–H bond length of $1{\cdot}42 \pm 0{\cdot}02$ Å., which is close to that of phosphine. The infra-red spectra of phosphonium bromide and phosphonium chloride have been investigated.[1021] The spectra were very similar to that of phosphonium iodide, and the same space group (*P*4/*nmm*) was proposed.[1021] The electronic structure of the phosphonium ion has been treated theoretically.[1019, 1032]

The $^1H$ and $^{31}P$ nuclear magnetic resonance spectra of phosphonium ions in strong acid solution have been observed.[1064] The proton chemical shift covers a range from $3{\cdot}61$–$3{\cdot}96\tau$; the phosphorus chemical shift is +217 p.p.m. from $P_4O_6$, and the spin-spin coupling constant has a range from 545·7–548·3 c/s.[1064] Proton NMR data have been reported for the $PH_2^-$ ion in liquid ammonia.[1305] The chemical shift is $11{\cdot}4$–$11{\cdot}5\tau$ and the coupling constant 139–140 c/s.[1065]

The infra-red spectra of phosphonium tetrachloroborate and trichlorofluoroborate have been reported, and the two active frequencies of the phosphonium ion found to lie in the regions 945–82 cm.$^{-1}$ and 2345–445 cm.$^{-1}$ [259]

The infra-red spectrum (vapour phase) of difluorophosphine has been assigned as follows[1074]: 2251/2240/2233 ($\nu_s$PH), 1016/1008 $\delta_{as}$PH, 851 ($\nu_s$PF), 838/825 ($\nu_{as}$PF), 367/348 $\delta_s$FPF. The proton NMR chemical shift in the vapour is $8{\cdot}7\tau$, which shows a complex coupling pattern.[1074] In the liquid the molecules are associated, giving a large change in chemical shift. The proton shift in the liquid is $2{\cdot}35\tau$, and the coupling constants $J_{PH}$ 182·4, $J_{FH}$ 41·7, $J_{PF}$ $1134 \pm 4$ c/s.[1074] Mass spectral data were also reported.[1074]

## PHOSPHORUS TRIHALIDES

The molecular structures of the phosphorus trihalides have been determined by electron diffraction[180]; the molecules are all pyramidal, as expected. For phosphorus trichloride and trifluoride bond lengths have been obtained also from microwave spectra. The available data on bond lengths and angles are given in Table III. The bond angles are typical of $p^3$–$sp^3$ hybrid bonding.

The Stark splitting of the microwave spectra[190–2] of phosphorus trifluoride has given a value for the molecular dipole moment of $1{\cdot}025 \pm 0{\cdot}009$ Debye units.[190–1]

The only trihalide which has been investigated by *X*-ray diffraction is the tri-iodide[187]; it crystallizes in a two-molecule hexagonal cell with $a = 7{\cdot}11$ Å., $c = 7{\cdot}24$ Å. The crystal is isomorphous with iodoform.

The nuclear quadrupole coupling constants have been determined for solid phosphorus trichloride[228]; at 77°K. two lines are observed for each chlorine isotope, showing that there are two non-equivalent chlorine positions in the lattice. A similar conclusion was reached in the case of the tribromide.[229]

The ultra-violet absorption spectra of phosphorus trichloride,[193–5, 1017] tribromide[194] and tri-iodide[196–7] have been investigated. Phosphorus trichloride shows a strong maximum at 217 mμ.[1017] Phosphorus tribromide shows two flat maxima at 2695 and 2495 Å. Phosphorus tri-iodide shows two maxima near 2850 and 3800 Å.

The Verdet constant of liquid phosphorus trichloride at 5780 Å. is $2{\cdot}52 \times 10^{-2}$.[198]

The Raman[165] and infra-red[215–8] spectra of phosphorus trifluoride have been investigated. The Raman and early infra-red work[165, 217] agree on the spectra, though not on assignment, but later infra-red work[216] shows that a band reported earlier at 531 cm.$^{-1}$ was absent. It seems likely that this band is due to an impurity. The frequencies are[216] as follow: 892 ($\nu_1$, *A*, symmetrical stretch), 860 ($\nu_3$, *E*, degenerate

*Table IV.—Force Constants of Phosphorus Trihalides*

| Molecule | Stretching force constant, $F_d$ millidynes/A. | Deformation force constant, $F_\alpha$ millidynes/A. | Reference |
|---|---|---|---|
| $PF_3$ | 5·342 ± 0·005 | 0·631 ± 0·009 | 1052 (and see 848, 216) |
| $PCl_3$ | 2·047 ± 0·040 | 0·343 ± 0·005 | 1052 (and see 826, 221, 848, 823) |
| $PBr_3$ | 1·83 | 0·23 | 1132 (and see 221) |
| $PI_3$ | 1·21 | 0·18 | 619 |
| $PFCl_2$ | P–F 4·10<br>P–Cl 2·70 | ClPF 0·25<br>ClPCl 0·61 | 752 |

rather than by racemization. Bond dipole moments and dipole moment derivatives have been calculated from the infra-red intensities for phosphorus trifluoride.[218] Values of about 1·07–1·20 Debye units, which were consistent among the different symmetry species and with the static molecular moment, were obtained for the bond dipole moments. The 'umbrella' frequency ($\nu_2$) of phosphorus trichloride is reported from the ultra-violet spectrum to lie between 230–65 cm.$^{-1}$ when the molecule is in an excited state.[224] A linear relation between the force constant of the phosphorus–halogen bond and the ionization potential has been suggested.[302]

Phosphorus nuclear magnetic resonance spectra have been determined for phosphorus trifluoride,[110, 225] difluoride chloride,[1050] fluoride dichloride,[1055] difluoride bromide,[1055] fluoride dibromide,[1055] difluoride iodide,[1051] trichloride,[110, 171, 226, 612] chloride dibromide,[834] bromide dichloride,[834] tribromide[110, 171, 226, 612] and tri-iodide.[110] The chemical shifts are respectively −97, −176, −224, −218, −255, −242·2, −219·4, −224·2, −226·9, −227·4, −178 p.p.m., relative to 85% orthophosphoric acid. The fluorine NMR spectra of the trifluoride,[225] difluoride chloride,[1057] fluoride dichloride,[1057] difluoride bromide,[1055] fluoride dibromide[1055] and difluoride iodide[1051] have been observed. Chemical shifts are respectively −43·4, −39·9, −20·7, −36·5, −6·2, 31·9 p.p.m. with respect to trifluoracetic acid. P–F spin-spin coupling constants are as follows: $PF_3$ 1405,[225] $PF_2Cl$ 1390–1380,[1051, 1057] $PFCl_2$ 1320,[1057] $PF_2Br$ 1388–95,[1055] $PFBr_2$ 1292–1301,[1055] $PF_2I$ 1037–1040.[1051] The decrease in shielding at the phosphorus atom in the order fluoride, iodide, chloride, bromide has been interpreted[110] as being due to a superposition of two opposing effects. These are the change in ionic character, which decreases the shielding in the order I, Br, Cl, F, and the effect of double bonding which tends to increase the shielding and which is expected to be greatest for fluorine, followed by chlorine. Arguments based on the bond lengths and angles and on the dipole moments, have also been advanced in support of multiple bonding in phosphorus trifluoride.[227] A dipole moment of 0·34 Debye units was obtained for phosphorus tri-iodide from dielectric constant measurements.[1056]

In a study of the electron-impact spectroscopy of phosphorus trichloride in a mass spectrometer,[1059] both positive and negative ($Cl^-$ and $PCl_2^-$) ion formation was reported and appearance potentials studied.

## Phosphorus Dihalides

The crystal structure of phosphorus di-iodide, $P_2I_4$, has been determined.[230] The molecule has a symmetrical trans-configuration, symmetry $C_{2h}$, with a P–P distance of 2·21 ± 0·06 A., and a P–I distance of 2·475 ± 0·028 A. The monomolecular cell is triclinic, space group $P\bar{1}$, with $a = 4·56$ A., $b = 7·06$ A., $c = 7·40$ A., $\alpha = 80° 12'$, $\beta = 106° 58'$ and $\gamma = 98° 12'$. The configuration of the $P_2I_4$ molecule in solution has been the subject of some disagreement.[1048–9, 1056, 1065–6] A staggered configuration was

*Table III.—Molecular Structures of Phosphorus Trihalides*

| Compound | Bond length A. | Interbond angle | Technique used | References |
|---|---|---|---|---|
| $PF_3$ | 1·537 ± 0·004 | 98·2 ± 0·6° | Electron diffraction | 181, 182, 1046 |
| | 1·546 ± 0·008 | 104° ± 3° (assumed) | Microwave spectra | 188 |
| $PCl_3$ | 2·00 ± 0·02 | 101° ± 2° | Electron diffraction | 181, 182, 183 |
| | 2·039 ± 0·014 | 100·27° ± 0·09° | Electron diffraction | 822, 1045 |
| | 2·043 ± 0·003 | 100°6′ ± 20′ | Microwave spectra | 189 |
| $PBr_3$ | 2·23 ± 0·01 | 100° ± 2° | Electron diffraction | 184 |
| $PI_3$ | 2·52 ± 0·01 | 98° ± 4° | Electron diffraction | 184 |
| | 2·43 ± 0·04 | 102·5° ± 2·5° | Electron diffraction | 185 |
| $PFCl_2$ | P–Cl 2·02 ± 0·03<br>P–F 1·55 ± 0·05 | FPCl = ClPCl = 102° ± 3° | Electron diffraction | 186 |

stretch, 487 ($\nu_2$ *A*, symmetrical deformation) and 344 cm.$^{-1}$ ($\nu_4$, *E*, degenerate deformation). For phosphorus trichloride the Raman spectra of the vapour,[824] liquid[199–204, 1047, 213–4, 824] (with depolarization ratio[202–3, 824]) and solid,[301] and the infra-red spectrum[215, 219–20, 1047, 1132] (including vapour, liquid and solid[1047]) have been determined. The four frequencies in the vapour phase have been reported as[824, 1047] $\nu_1$ 'A' 514 (Raman); $\nu_3$ 'E' 482 (Raman), 507 (IR); $\nu_2$ 'A' 256 (Raman) 259 (IR); $\nu_4$ 'E' 184 (Raman), 187 (IR). The frequencies of phosphorus tribromide determined from the Raman spectrum[201–2, 204] are 400 ($\nu_3$), 380 ($\nu_1$), 162 ($\nu_2$) and 116 ($\nu_4$) cm.$^{-1}$ The frequencies determined from the infra-red spectrum[1132] are 392 ($\nu_3$), 392 ± 5 ($\nu_1$), 161 ($\nu_2$) and 116 ($\nu_4$) cm.$^{-1}$ The Raman[619, 898] and infra-red[1048, 1049] spectra of phosphorus tri-iodide have been determined. The fundamental frequencies[1049] are 328 ($\nu_3$), 306 ($\nu_1$), 112 ($\nu_2$), 80 ($\nu_4$) cm.$^{-1}$ Raman[209–12] and vapour-phase infra-red[1055] spectra have been reported for $PFCl_2$ and $PFBr_2$. Observed Raman frequencies are as follow ($p$ = polarized): $PFCl_2$, 200 ($p$), 271, 327 ($p$), 496, 524 ($p$), 827 ($p$); $PFBr_2$, 126 ($p$), 220, 257 ($p$), 393, 421 ($p$), 817 ($p$) cm.$^{-1}$ The infra-red spectrum of $PF_2Br$[1055] is as follows: 391, 459, 849, 858 cm.$^{-1}$ The infra-red[1050] and Raman[209–12] spectra of $PF_2Cl$ exhibit fundamentals[1050] 864 ($\nu_sPF_2$), 852 ($\nu_{as}PF_2$), 545 ($\nu$PCl), 411 ($\delta_s$FPF), 308 ($\delta$PCl) cm.$^{-1}$ Approximate stretching force constants of 4·81 (PF) and 2·87 millidynes/A. (PCl) were obtained. Raman spectra have also been reported for PFClBr,[209–12] $PCl_2Br$ and $PClBr_2$,[200, 204–8, 898–900] $PBrI_2$ and $PBr_2I$.[898] The infra-red spectrum of $PF_2I$ as far as 200 cm.$^{-1}$ has been reported,[1051] with fundamentals at 850 ($\nu_sPF_2$), 845 ($\nu_{as}PF_2$), 412 ($\delta_s$FPF), 378 ($\nu_s$PI) cm.$^{-1}$ with $\delta_{as}PF_2$ and $\delta$PI expected below 200 cm.$^{-1}$ The observed frequencies of PFClBr are as follow: 161, 231, 302, 415, 500, 822 cm.$^{-1}$ Force constants have been worked out (Table IV) for phosphorus trifluoride,[216–7, 221–3, 848, 1052–3] fluoride dichloride,[752] trichloride,[221–2, 823, 848, 1052–4, 1132–3] tribromide[221–2, 1053, 1132] and tri-iodide.[619, 1053] For $PF_3$ and $PCl_3$ centrifugal distortion constants obtained from millimetre wave spectra have been used in conjunction with the vibrational data to give more accurate force constants.[1052]

The complete potential function for the trichloride[823] has been derived from the vibration frequencies[824] and vibrational amplitudes[822] in the vapour phase. The energy barriers for inversion[172] are respectively 45·1, 68·1 and 52·7 kcal./mole. for the fluoride, chloride and bromide respectively, and the separation of optically active trihalides at room temperature appears to be limited by chemical decomposition originally suggested[1056] on the basis of the dipole moment (0·45 Debye units, from dielectric constant measurements). This was supported by infra-red work[1048, 1066] in which four IR-active PI stretching fundamentals were assigned at 354, 332, 328 and 313 cm.$^{-1}$ thereby excluding the *trans*-$C_{2h}$ structure which would give only two infra-red active PI modes. Later workers,[1048, 1065] on the basis of Raman as well as infra-red data, suggested that 354 cm.$^{-1}$ was an overtone, and that 332 cm.$^{-1}$ was of doubtful validity, and concluded from the mutual exclusion of infra-red and Raman spectra that the molecule retained its *trans*-$C_{2h}$ structure in solution. The $^{31}$P NMR shift of $P_2I_4$ in $CS_2$ solution is $-108$ p.p.m. relative to 85% orthophosphoric acid.[110, 1259]

The infra-red and Raman spectra of diphosphorus tetrachloride, $P_2Cl_4$, have been assigned[1047] on the basis of a *trans*-configuration of $C_{2h}$ symmetry, similar to the tetra-iodide, in the solid liquid and vapour. Assignments were as follow: $a_g$ (Raman, *p*), 494, 410, 238, 149; $a_u$ (IR), 501, 201, 91; $b_g$ (Raman), 480, 189; $b_u$ (IR), 508, 275, 139 cm.$^{-1}$ [1047] The $^{31}$P chemical shift of $P_2Cl_4$ is $-155$ p.p.m. relative to 85% $H_3PO_4$.[1067]

A *trans*-configuration has also been suggested[1068-9] for diphosphorus tetrafluoride on the basis of infra-red[1068-71] and Raman[1068-9] data. Assignments[1068] were as follow: IR 847/839, 834/829 ($\nu$PF), 365, 361 ($\phi PF_2$); Raman 825 *p*, 803 ($\nu$PF), 541 *p* ($\nu$PP), 453 ($\omega PF_2$), 377 ($\delta PF_2$) cm.$^{-1}$ The NMR spectrum[1068, 1070] is a complex $X_2AA'X_2$ pattern. The chemical shifts[1068] are: $^{31}$P, $-226$ p.p.m. relative to 85% $H_3PO_4$; $^{19}$F, 37·6 p.p.m. relative to trifluoracetic acid. The P–F coupling constant is about 1100 c/s.[1068] The $X_2AA'X_2'$ pattern is more complex than that derived theoretically for this system,[1072] probably because $J_{FPPF'} \neq 0$.[1068] The compound showed an electron spin resonance spectrum, attributed to $PF_2$ radicals, with a *g*-value of 2·00129.[1068] Mass spectral data have been reported.[1070]

The compound $\mu$-oxobisdifluorophosphine, $F_2POPF_2$, identified by NMR, infra-red and mass spectrometry, has been reported.[1068, 1070, 1155] The $^{31}$P chemical shift is $-114·6$ relative to orthophosphoric acid[1155]; the $^{19}$F spectrum was analysed as an $X_2AA'X_2'$ system,[1068, 1070] with parameters[1068] $\delta_F = -39·9$ p.p.m. (relative to trifluoracetic acid), $J_{PF} = 1358$, $J_{PF} = -14$, $J_{PP} = 4$ c/s. $J_{FF'}$ was assumed to be zero. Infra-red bands were assigned[1068] at 682 ($\nu_s$POP), 976 ($\nu_{as}$POP), 842/853/863 ($\nu$PF).

### Adducts of Phosphorus Trihalides and Dihalides

The Raman spectra of the liquid compounds phosphorus trifluoride-borane, $F_3P,BH_3$, and phosphorus trifluoride-borane-$d_3$, have been determined at $-80$°C.[643] and polarization measurements made. The spectra were assigned on the basis of a staggered $C_{3v}$ configuration. The P–B stretching frequency was assigned as 607 cm.$^{-1}$ (572 cm.$^{-1}$ in the deuterated compound).

The compound titanium phosphorus chloride, $TiPCl_7$ (presumably $TiCl_4,PCl_3$), crystallized from a mixture of titanium tetrachloride and phosphorus trichloride, is orthorhombic, space group *Pbca*, with $a = 12·61$, $b = 13·59$, $c = 12·70$ A., $Z = 8$.[644] The similar compound, titanium phosphorus bromide ($TiP_2Br_{10}$ or $TiBr_4,2PBr_3$), prepared by addition of titanium tetrachloride to phosphorus tribromide, is orthorhombic, space group $P222_1$ or $P2_12_12$, with $a_0 = 14·84$, $b_0 = 8·61$, $c_0 = 7·24$ A., $Z = 2$.[645]

The Raman spectrum of tetrakis(trifluorophosphine) nickel has been determined.[639-40] The numbers of polarized and depolarized lines are in agreement with a regular tetrahedral arrangement (point group *Td*), and are assigned on this basis. The totally symmetric ($A_1$) P–F stretching vibration appears at 954 cm.$^{-1}$, and the corresponding $E$ and $F_2$ vibrations at 851 and 888 cm.$^{-1}$ respectively. The Ni–$P_4$ symmetrical stretching ($A_1$) vibration is at 195 cm.$^{-1}$, and the corresponding asymmetrical ($F_2$) vibration at 219 cm.$^{-1}$ Factorized valence force constants were calculated for the totally symmetric species only, with results of 7·73 millidynes/A. for P–F stretching, 2·71 millidynes/A. for Ni–P stretching and $k\delta/r^2 = 0·53$ millidynes/A. for the $PF_3$ 'umbrella' deformation. The Ni–P force constant is lower than expected, as the bond might be expected to have some double-bond character arising from back co-ordination on to vacant *d* orbitals on the phosphorus. Some infra-red data for hexakis(trifluorophosphine) chromium have been reported.[1058] P–F stretching vibrations were observed at 916 and 851 cm.$^{-1}$

The crystal structure of the compound AuCl,PCl$_3$ has been determined.[835] The unit cell is monoclinic, with space group $P2_1/c$, and $a = 7{\cdot}23$ A., $b = 14{\cdot}62$ A., $c = 6{\cdot}19$ A., $Z = 4$. Molecules of Cl$_3$P → Au–Cl have almost linear P → Au–Cl linkages. The Au–P distance is 2·19 A., and the PCl distances of 1·84, 1·98 and 2·07 A. appear to be on average shorter than in free PCl$_3$, supporting a suggestion[836] that stronger bonds go with higher co-ordination. The accuracy of the determination, however, is insufficient for this difference to be significant.

The infra-red spectra of the solid adducts PI$_3$,BBr$_3$, P$_2$I$_4$,2BBr$_3$ [1048] and PI$_3$, BI$_3$ [1048, 1073] have been reported. B–Br stretching vibrations were assigned at around 681 ($^{10}$B) and 647 ($^{11}$B) cm.$^{-1}$, BI stretches at 590/598 ($^{10}$B) and 564 ($^{11}$B) cm.$^{-1}$, PI stretches at 302–361 cm.$^{-1}$, and P–B stretches at 384–412 cm.$^{-1}$ [1048] An approximate P–B stretching constant of 1·0 millidynes/A. in PI$_3$,BI$_3$ has been reported.[1073]

## PHOSPHORUS PENTAHALIDES AND HALOPHOSPHORANES

The structures of phosphorus pentafluoride[186, 254, 1046, 1075, 1313] and pentachloride[232–3] in the vapour state have been determined by electron diffraction; the molecules are trigonal bipyramids. An electron diffraction study[186] of phosphorus dichloride trifluoride proposed a structure with the three fluorine atoms equatorial and the two chlorines axial but recent work (below) has shown this to be erroneous. Bond lengths are as follow:

| Molecule | Bond | Length A. | Reference |
|---|---|---|---|
| PF$_5$ | Axial PF | $1{\cdot}549 \pm 0{\cdot}005$ | 1046 |
| | | $1{\cdot}577 \pm 0{\cdot}005$ | 1075 |
| | Equatorial PF | $1{\cdot}499 \pm 0{\cdot}004$ | 1046 |
| | | $1{\cdot}534 \pm 0{\cdot}004$ | 1075 |
| PCl$_5$ | Axial PCl | $2{\cdot}19 \pm 0{\cdot}06$ | 232,233 |
| | Equatorial PCl | $2{\cdot}04 \pm 0{\cdot}06$ | |

The crystal structures of solid phosphorus pentachloride[234–6] and pentabromide[237–8] have been determined. The molecular structures in the solid are quite different from those in the vapour phase. Solid phosphorus pentachloride is composed of alternate tetrachlorophosphonium, PCl$_4^+$, and hexachlorophosphate, PCl$_6^-$, ions. These crystallize in a tetragonal four-molecule cell with $a = 9{\cdot}22$ and $c = 7{\cdot}44$ A.; the space group is $P4/n$. The P–Cl bond lengths are 1·97 A. in the tetrachlorophosphonium ion, which is tetrahedral, and 2·04–2·08 A. in the hexachlorophosphate ion which is approximately a regular octahedron. Solid phosphorus pentachloride prepared by sublimation is stated to have a different structure, similar to that of the compound PCl$_{4{\cdot}67}$Br$_{0{\cdot}33}$.[719] The chlorine nuclear quadrupole resonance of PCl$_5$ has been examined.[257] Three lines were reported but the results have apparently not been correlated with the crystal structure. Chlorine nuclear quadrupole resonance data have been obtained for the molecular forms of phosphorus tetrachloride fluoride, trichloride difluoride, dichloride trifluoride[1076–7] and chloride tetrafluoride.[1078] These show that in the solid state the molecules retain the trigonal bipyramidal structures deduced by spectroscopic methods (below) for the liquid and gaseous states. For PCl$_4$F two $^{35}$Cl resonance signals are observed at 32·54 (triplet, intensity 3) and 28·99 (intensity 1) Mc/s, assigned to equatorial and axial chlorines respectively, indicating that the single fluorine is axial. PCl$_3$F$_2$, PCl$_2$F$_3$, and PClF$_4$ all give signals assignable to equatorial chlorines only at 31·26/31·89 Mc/s, 31·49 and 32·14 Mc/s respectively, indicating that the fluorines adopt axial positions preferentially.[1076–8]

Solid phosphorus pentabromide is composed of tetrabromophosphonium ions, $PBr_4^+$, and bromide ions, $Br^-$, which crystallize in an orthorhombic four-molecule cell with $a = 5{\cdot}62$, $b = 16{\cdot}91$, $c = 8{\cdot}29$ A. The space group is *Pbcm.* The tetrabromophosphonium ion is a slightly irregular tetrahedron, with P–Br bond lengths of 2·02–2·18 A. The shortest $Br^-$–P distance is 4·3 A.[238]

An approximate structure has been suggested[719] for the compound $PCl_{4\cdot67}Br_{0\cdot33}$. This crystallizes in a face-centred cubic structure with a cell edge of 12·38 A., containing twelve 'molecules', i.e. the cell contents are $P_{12}Cl_{56}Br_4$. The suggested structure is a cæsium chloride-type array of $8PCl_4^+$, $4PCl_6^-$ and $4Br^-$ ions.

The infra-red spectrum of phosphorus pentafluoride vapour[217, 249, 1079–84] and the Raman spectrum of the liquid[1079–81, 1083] have been studied. The spectra confirm the trigonal bipyramidal structure.[1079, 1083] A normal co-ordinate calculation was used[1083] to investigate the rates of internal exchange[1085] of axial and equatorial fluorine atoms. Bond stretching force constants have been calculated[839, 1082, 1087–8] and are 6·58 and 3·13 millidynes/A. for equatorial and axial P–F bonds respectively.[1082] Assignments are as follows[1083]: 1025 (Raman, IR, $\nu_{as}PF_3$ $E'$), 946·6 (IR, $\nu_{as}PF_2$ $A_2''$), 817 (Raman, *p*, $\nu$PF in phase $A_1'$), 640 (Raman, *p*, $\nu$PF ax/eq out of phase $A_1'$), 575 (IR, $PF_3$ umbrella $A_2''$), 532 (Raman, IR in plane bend, $E'$), 514 (Raman, degen. $PF_3$ bend, $E''$), 300 (IR, degen. axial bend $E'$) $cm.^{-1}$

The infra-red and Raman spectra of phosphorus chloride tetrafluoride[1078] support a trigonal bipyramidal structure of $C_{2v}$ symmetry with an equatorial chlorine atom. Assignments are as follows[1078]: 921 (Raman, IR, $\nu PF_2$, $b_1$), 903 (Raman, IR, $\nu PF_2'$, $b_2$), 895 (Raman, *p*, IR, $\nu_s PF_2$, $a_1$), 691 (Raman, *p*, IR, $\nu_s PF_2'$, $a_1$), 560 (Raman, IR, out-of-plane bend, $b_2$), 510 (Raman, *p*, IR, $\gamma PF_2$, $a_1$), 490 (Raman, IR, $PClF_2$ in-plane bend, $b_1$), 434 (Raman, *p*, IR, $\nu$PCl, $a_1$), 356 (Raman, IR, $PF_2$ twist and rock, $a_2 + b_2$?), 144 (Raman, *p*, IR, $PF_2'$ bend, $a_1 + b_1$?) $cm.^{-1}$

The infra-red[720, 1079, 1086] and Raman[1079] spectra of phosphorus dichloride trifluoride have been studied. Different workers[1079, 1086] agree in rejecting the $D_{3h}$ axial-chlorine structure originally proposed from electron diffraction work[186] in favour of a structure of $C_{2v}$ symmetry with two fluorine atoms axial. However, there is considerable disagreement about the vibrational assignments[1079, 1086]; those of the later workers[1086] are as follows: 925 ($PF_2$eq. stretch $a_1$), 895 ($PF_2'$ax. asym. stretch $b_2$), 667 ($\nu_{as}PCl_2$, $b_1$), 650 ($PF_2$ax. sym. stretch, $a_1$), 562 (PF bend, $b_1$), 490 (PF bend, $b_2$), 429 ($PF_2$ax. bend, $a_1$), 407 ($\nu_s PCl_2$, $a_1$), 337 ($PF_2'$ wag, $b_1$) $cm.^{-1}$ Low-frequency assignments[1079] are 368 ($a_2$), 124 ($a_1 + b_2$?) $cm.^{-1}$

The infra-red and Raman spectra of phosphorus trichloride difluoride[1079] are consistent with a trigonal bipyramidal structure of $D_{3h}$ symmetry, with the fluorine atoms in axial positions. Assignments are as follows[1079]: 867 ($\nu_{as}PF_2$, IR, $a_2''$), 633 ($\nu_s PF_2$, Raman, *p*, $a_1'$), 625 ($\nu_{as}PCl_3$, Raman, IR, $e'$), 404 ($\delta PCl_3$, Raman, IR, $e'$), 387 (Raman, *p*, $\nu_s PCl_3$), 357 (Rocking, Raman, $e''$), 328 ($\delta PCl_3$, IR, $a_2''$), 122 (Raman, IR, $PF_2$ax. bend, $e'$) $cm.^{-1}$

The infra-red and Raman spectra of the molecular form of phosphorus tetrachloride fluoride[1079] have been interpreted in terms of a $C_{3v}$ structure, with the fluorine atom on an axial site. Assignments are: 778 ($\nu$PF, $a_1$), 601 ($\nu_{as}PCl_3$, $e$), 422 ($\nu_s PCl_3$, $a_1$), 388 ($\nu$PCl, $a_1$), 339 ($\delta_{as}PCl_3$, $e$), 297 (Rock/bend, $e$), 265 ($\delta_s PCl_3$, $a_1$), 110 (Rock/bend, $e$).

The ionic compound of composition $PCl_4F$ has also been studied by infra-red spectroscopy.[1089] It was suggested that the structure should be formulated as $PCl_4^+$ $PCl_4F_2^-$ rather than as $PCl_4^+F^-$.

Force constants have been reported[1088] for the series of phosphorus chlorofluorides $PF_4Cl$, $PF_3Cl_2$, $PF_2Cl_3$ and $PFCl_4$. Axial PF stretching constants are 4·62, 4·37, 4·10 and 3·92 millidynes/A. respectively. Equatorial PCl stretching constants are 3·45, 3·45, 3·07 and 3·07 millidynes/A. respectively. Equatorial PF stretching constants in $PF_4Cl$ and $PF_3Cl_2$ are 6·25 and 5·82 millidynes/A. respectively. The axial PCl stretching constant in $PFCl_4$ is 1·94 millidynes/A.[1088]

The Raman[1088] and infra-red[1088, 1090] spectra of trifluorophosphorane, $PH_2F_3$, have been studied. It was concluded[1088] that in the gas phase the molecule was a trigonal bipyramid of symmetry $C_{2v}$ with the two fluorine atoms axial. In condensed phases molecules associate through fluorine bridges.[1088] Assignments[1088] for the vapour phase spectra were as follows: 2538 ($\nu_s PH_2$, $A_1$), 2465 ($\nu_{as} PH_2$, $B_1$), 1292 ($\delta PH_2$, $A_1$), 1026 ($\nu_{as} PF_2'$, $B_2$), 995 ($\nu_s PF$, $A_1$), 867 ($\gamma PH_2F$, $B_2$), 820 ($\nu_s PF_2'$, $A_1$), 765 ($\delta FPH_2$, $B_1$), 655 ($\delta HPF'$, $A_2$), 471 ($\delta PF_2'$, $A_1$), 389 ($\delta_{as} PF_2'$, $B_1$), 329 ($\delta PF_2/PHF$, $B_2$). Approximate valence force constants were worked out, as follows[1088]: PH stretching 3·59, $PF_{(ax)}$ 7·18, $PF_{(eq)}$ 5·77 millidynes/A.

The infra-red spectrum of tetrafluorophosphorane, $PHF_4$, has been reported.[1090] The principal bands are at 2478, 1027, 890, 881, 866, 832, 538 and 532 cm.$^{-1}$

The Raman spectrum of phosphorus pentachloride has been extensively investigated in the solid,[239–42] liquid[240–1] and vapour[241] phases, and in solution.[241, 243] The spectra confirm the trigonal bipyramidal structure and the different structure in the solid.[240–1, 244–5] Infra-red studies in various solvents have led to the conclusion that phosphorus pentachloride exists as the molecular form in solution in phosphorus oxychloride, benzene, *cyclo*hexane and dichlorethane, the ionic form in acetonitrile solution (but the Raman[1110] spectrum suggests that a small proportion of the molecular species is present), and as a dimer, $P_2Cl_{10}$, in carbon tetrachloride solution.[1091] Force constants have been worked out.[242–3, 246–7] The infra-red[259, 1092–3] and Raman[242, 1092] spectra of solid phosphorus pentachloride have recently been reported, together with the spectra of other compounds containing the tetrachlorophosphonium ion. In the latest work[243, 1092–4] on the vibrational spectra of molecular phosphorus pentachloride, the infra-red[1092–3] spectrum was observed in the vapour and solution and the Raman spectrum[1092, 1094] in solution, with measurement of the depolarization ratios. There has been considerable disagreement[243, 1092–5, 1110–11] over the vibrational assignments. Force constants have been calculated,[243, 1087–8, 1095–7] but apparently none of the calculations used the latest assignments[1110–1] (see Table V*a*). Table V also gives assignments[1092, 1110] for the tetrachlorophosphonium and hexachlorophosphate ions in ionic phosphorus pentachloride. The latter were obtained[1110] from phosphorus pentachloride in the solid and in acetonitrile solution, and also from related derivatives such as $Et_4NPCl_6$ and pyH.$PCl_6$.pyHCl. Force constants[1098–9] and mean amplitudes of vibration[1100–1] have been calculated for the tetrachlorophosphonium ion.

The infra-red spectrum of phosphorus trifluoride dibromide has been reported[1086] and assigned as follows (by comparison with that of $PF_3Cl_2$) on the basis of a trigonal bipyramidal structure of symmetry $C_{2v}$, with equatorial bromine atoms: 913 ($\nu$PFeq., $a_1$), 878 ($\nu_{as} PF_2'$ ax., $b_2$), 607 ($\nu_s PF_2'$ ax., $a_1$), 587 ($\nu_{as} PBr_2$, $b_1$), 510 ($\delta$PF, $b_1$), 458 ($\delta$PF, $b_2$), 420 ($\delta PF_2'$ ax., $a_1$), 335 ($\delta PF_2'$, $b_1$) 318 ($\nu_s PBr_2$, $a_1$) cm.$^{-1}$

The Raman spectrum of solid phosphorus pentabromide has been investigated.[248] The following frequencies were assigned to the tetrabromophosphonium ($PBr_4^+$) ion: 72 ($E$), 140 ($F_2$), (both deformation modes), 227 ($A_1$) and 474 cm.$^{-1}$ ($F_2$) (both stretching modes). Force constants[248, 1098] and mean amplitudes of vibration[1101] have been calculated. The stretching force constant of the PBr bond, calculated from these frequencies using a Urey–Bradley force field, is 2·19 millidynes/A.[248]

The bonding in the phosphorus pentahalides has been discussed by several authors.[250–2] It is considered[252] that the phosphorus *d* orbitals are normally too diffuse to take part in bonding and can only take part in the formation of $sp^3d$ hybridization, as in the pentahalides, when they are contracted by the influence of electronegative elements bonded to the phosphorus. The bonding in the chloride fluorides and other derivatives with mixed substituents has received particular attention,[1106–9] and attempts have been made to explain the structural features of these molecules on the basis of electron-pair repulsion theories[1106] and Hückel molecular-orbital calculations.[1107–8] These have suggested[1108] that the stability of the observed isomers is a function of $\sigma$-bonding rather than $\pi$-bonding or *d*-orbital participation although these are both present. The equatorial phosphorus orbitals are stated to be more electronegative, thereby concentrating the *s*-orbitals of the

*Table V*

(*a*) Fundamental frequencies of phosphorus pentachloride[243, 1110]

| Frequency cm.$^{-1}$ | Assignment |
|---|---|
| 100 | $E'$ $PCl_3$ in-plane bending |
| 261 | $E''$ $Cl_{ax}PCl_{ax}$ linear rocking |
| 273 | $E'$ $Cl_{ax}PCl_{ax}$ linear bending |
| 282 | $A_1'$ $PCl_{ax}$ symmetrical stretching |
| 300 | $A_2''$ $PCl_3$ out-of-plane bending |
| 393 | $A_1'$ $PCl_{eq}$ symmetrical stretching |
| 448 | $A_2''$ $PCl_{ax}$ unsymmetrical stretching |
| 581 | $E'$ degenerate $PCl_3$ stretching |

(*b*) Fundamental frequencies of the tetrachlorophosphonium ion[1092]

| Frequency cm.$^{-1}$ | Assignment |
|---|---|
| 171 | $E$ Deformation |
| 252 | $F_2$ Deformation |
| 459 | $A_1$ PCl stretching |
| 658 | $F_2$ PCl stretching |

(*c*) Fundamental frequencies of the hexachlorophosphate ion[1110]

| Frequency cm.$^{-1}$ | Assignment |
|---|---|
| 285 | $F_{1u}$ Deformation (IR) |
| 238 | $F_{2g}$ Deformation (Raman) |
| 262–283 | $E_g$ PCl stretching (Raman) |
| 353–360 | $A_{1g}$ PCl stretching (Raman, *p*) |
| 444–454 | $F_{1u}$ PCl stretching (IR)<br>(see also ref. 242) |

phosphorus and strengthening these bonds relative to the axial ones as reflected by the structural and force constant data. Electronegative substituents then tend to favour the (electropositive) axial bonds, accounting for the occurrence of the observed isomers.[1108]

The ultra-violet absorption spectra of phosphorus pentachloride[194, 253] and pentabromide[194] have been reported. The pentachloride shows continuous absorption below about 2130 A., with a maximum at 2310 A.[194]; the pentabromide shows a maximum at about 2744 A.

The dipole moments of phosphorus tetrafluoride chloride[1078] (0·78 Debye units) and trifluoride dichloride[1105] (0·68 Debye units, in agreement with the $C_{2v}$ symmetry) have been determined from the temperature variation of the gas-phase dielectric constant. The same method has been used to confirm that the dipole moment of phosphorus difluoride trichloride is zero.[1105] The dipole moment of phosphorus fluoride trichloride is 0·21 Debye units, from measurements on the gas-phase nonresonant absorption at microwave frequencies.[1105]

The fluorine nuclear magnetic resonance in phosphorus pentafluoride[225] shows a single chemical shift, suggesting that the five fluorine atoms might be equivalent; an earlier report[753] suggesting non-equivalence has been discounted. In view of the trigonal bipyramidal structure such equivalence would be surprising. Suggested explanations have included intra-[1085] and inter-molecular fluorine exchange and 'accidental' equivalence of chemical shifts.[255] However, recent work[1083] on the vibrational potential function has enabled the height of the barrier to intramolecular fluorine exchange to be calculated, and has predicted exchange rates which suggest that the axial/equatorial NMR shifts are unlikely to be resolved at low temperatures. These shifts have, however, been resolved in phosphorus trifluoride dichloride and dibromide (below).

The fluorine NMR spectrum of phosphorus tetrafluoride chloride in *iso*pentane solution is reported[1084] to show a single doublet at +23·5 p.p.m. from $CCl_3F$, with a P–F coupling of 1000 c/s. Since the NQR and vibrational data (above) indicate a trigonal bipyramidal structure of $C_{2v}$ symmetry with an equatorial chlorine atom, these values are presumably averages resulting from intramolecular exchange of axial and equatorial fluorine atoms.

The fluorine NMR spectrum of phosphorus trifluoride dichloride at 25°C.[1057, 1102–4] likewise shows a single fluorine chemical shift (−108 to 112 p.p.m. from trifluoroacetic acid) and a single PF coupling constant (1048–50 c/s). In solution below −120°C., however,[1077, 1102–3] the intramolecular fluorine exchange showed sufficiently for the signals from axial and equatorial fluorines to be resolved. Axial fluorines have a shift of −144 p.p.m. relative to trifluoroacetic acid.[1102] with a P–F coupling constant of 1023 c/s. Equatorial fluorines have a shift of −36 p.p.m. and a coupling constant of 1085 c/s. The axial-equatorial fluorine coupling is 142 c/s.[1102] The activation energy for intramolecular fluorine exchange has been calculated from the variation of the NMR spectrum with temperature, and found to be 7·2 kcal./mole.[1102]

Phosphorus difluoride trichloride shows a fluorine NMR spectrum[1057, 1077] with a simple doublet ($J_{PF} = 1045$ c/s) which does not change in appearance or in chemical shift (−191·8 p.p.m. relative to trifluoroacetic acid) from −22°C. to 140°C., indicating a single type of fluorine environment (axial) with no intramolecular fluorine exchange, in agreement with the vibrational and NQR data (above). In phosphorus fluoride tetrachloride the situation is similar,[1057, 1077] with a shift of −220·0 p.p.m. and a coupling constant of 996 c/s.[1057]

The proton and fluorine NMR spectra of trifluoro- and tetrafluorophosphorane have been studied.[1090] The results suggested that, at the lowest temperatures studied, both molecules are undergoing intramolecular fluorine exchange, the PH and PF coupling being retained. The temperature dependence of the spectra of trifluorophosphorane also suggests that this molecule is self-associated in the condensed state, in agreement with the conclusions from the vibrational data.[1088] The chemical shifts range from 2·68–3·10 $\tau$ and 29–48 p.p.m. relative to $CCl_3F$, depending on the temperature. The coupling constants are $J_{PH} = 841$–894 c/s, $J_{PF} = 770$–860 c/s.[1090] For tetrafluorophosphorane at higher temperatures an intermolecular exchange with PF bond breakage is proposed[1090] to explain the NMR data. Chemical shifts are 2·48–2·62 $\tau$ and 47·1–50·2 p.p.m. relative to $CCl_3F$. Coupling constants are $J_{PH}$ 1075–1093 c/s, $J_{PF}$ 892–980 c/s and $J_{HF}$ 91 c/s.[1090]

The fluorine NMR spectrum of phosphorus trifluoride dibromide[1102–4] shows resolution of the axial and equatorial fluorine signals below −120°C. Chemical shifts of axial and equatorial fluorines are −181 and −43 p.p.m. respectively relative to trifluoroacetic acid. PF coupling constants are 1141 c/s (axial) and 1143 c/s (equatorial). The $F_{ax.}F_{eq.}$ coupling constant is 124 c/s. The exchange activation energy was deduced to be 7·2 kcal./mole.[1102]

Phosphorus nuclear magnetic resonance spectra have been observed for $PF_5$ (vapour and liquid[225]) but the chemical shift has apparently not been reported. The phosphorus chemical shift in phosphorus fluoride tetrachloride is $-56 \pm 2$ p.p.m. relative to 85% orthophosphoric acid.[1057] The chemical shifts of trifluoro- and tetrafluorophosphorane are reported to be approximately +180 and +191 p.p.m. respectively from trimethyl phosphate.[1090] The phosphorus NMR spectrum of molecular phosphorus pentachloride has been determined,[171] and the spectrum of solid $PCl_5$ has been examined under high resolution by an elegant technique[256, 971] and the chemical shifts of the $PCl_4^+$ and $PCl_6^-$ ions resolved. Chemical shift data for the various phosphorus–chlorine containing species (relative to 85% orthophosphoric acid) are as follow: $PCl_3$ −219, $PCl_4^+$ −96, $PCl_5$ +80 and $PCl_6^-$ +281 p.p.m. The chemical shift in phosphorus oxychloride solution of the $PCl_6^-$ ion (in the compound $[Ph_2ClP{=}N{-}PCl_3]^+PCl_6^-$ is reported to be 305 p.p.m. relative to 85% $H_3PO_4$.[1109]

## TETRACHLOROPHOSPHONIUM COMPOUNDS

The crystal structure of tetrachlorophosphonium dichloroiodide, $PCl_4^+.ICl_2^-$, has been determined.[258] This compound crystallizes in a tetragonal two-molecule cell with $a=9{\cdot}26$ A., $c=5{\cdot}68$ A. The space group is $P\bar{4}2_1m$. The bond length of the $PCl_4^+$ tetrahedra is 1·98 A. which is in good agreement with that in solid $PCl_5$. An infra-red spectrum attributed to the tetrachlorophosphonium ($PCl_4^+$) ion has been resolved from the spectra of tetrachlorophosphonium tetrachloroborate, $PCl_4^+.BCl_4^-$, chlorotrifluoroborate, $PCl_4^+.BF_3Cl^-$, and chlorosulphonate, $PCl_4^+.SO_3Cl^-$.[259] The spectrum was partly assigned, but the band at 584 cm.$^{-1}$ is probably[1093] due to phosphoryl chloride. Some infra-red data have also been reported[1093] for tetrachlorophosphonium hexachloroantimonate, $PCl_4^+.SbCl_6^-$.

It has been proposed,[1110] on the basis of infra-red and other evidence, that the compound $PCl_5,AsCl_5$, previously formulated as $AsCl_4^+.PCl_6^-$, should in fact be formulated as $PCl_4^+.AsCl_6^-$.

## HEXAFLUOROPHOSPHATES

The crystal structures of hexafluorophosphoric acid, $HPF_6,H_2O$, and its sodium, potassium, ammonium, cæsium, rubidium, silver and thallium salts have been investigated.[341–6, 1112] There is large variation among the dimensions reported for the hexafluorophosphate ion in the different compounds. The acid[341] is cubic, space group *Im*3*m*, with a unit cell having $a=7{\cdot}679$ A. and containing two molecules. The six fluorine atoms lie around the phosphorus atom in an octahedral arrangement; the P–F distance is reported to be 1·73 A. The hexafluorophosphate ion lies at the centre of a cage of 24 oxygen atoms. The structure of sodium hexafluorophosphate monohydrate, which has been investigated in considerable detail,[342] is orthorhombic, space group *Imma*, with $a=7{\cdot}962$ A., $b=10{\cdot}594$ A., $c=6{\cdot}116$ A., $Z=4$. Four of the fluorine atoms lie in a plane around the phosphorus atom, with a P–F distance of 1·58 A.; the other two lie perpendicular to this plane on opposite sides of the phosphorus atom and 1·73 A. from it. In anhydrous sodium hexafluorophosphate, $NaPF_6$,[343] the sodium and hexafluorophosphate ions are arranged in a sodium chloride-like array, with the orientations of the hexafluorophosphate ions disordered, giving space group symmetry *Fm*3*m*. The unit cell has $a=7{\cdot}61$ A. and contains four molecules. The $\alpha$-form of potassium hexafluorophosphate, $KPF_6$,[344] which is stable below about $-25$°C., has a tetramolecular cubic cell with $a=7{\cdot}71$ A. Hexafluorophosphate ions with a P–F distance of 1·58 A. lie on a sodium chloride-like array of space group *Pa*3, as in sodium hexafluoroantimonate, disproving an earlier suggestion[345] that tetrafluorophosphonium ions are present. Ammonium and cæsium hexafluorophosphates are isomorphous with $\alpha$-potassium hexafluorophosphate.[344] Thallous hexafluorophosphate is also cubic with $a=7{\cdot}94$ A.[346] Other hexafluorophosphate compounds for which *X*-ray data have been reported[154] are hexammine-cobaltous hexafluorophosphate, $Co(NH_3)_6(PF_6)_2$, and hexammine-nickel hexafluorophosphate, $Ni(NH_3)_6(PF_6)_2$, (both are cubic with the potassium hexachloroplatinate, $K_2PtCl_6$, structure, $Z=4$, and $a=11{\cdot}942$ and 11·912 A. respectively), and hexammine-cobaltic hexafluorophosphate, $Co(NH_3)_6(PF_6)_3$, which is cubic with the ammonium hexafluoroferrate, $(NH_4)_3FeF_6$, structure; the unit cell has $a=11{\cdot}670$ A., with space group *Fm*3*m*, and contains four molecules. Tetrachlorophosphonium hexafluorophosphate, $[PCl_4]^+[PF_6]^-$, is reported[718] to be isomorphous with solid phosphorus pentachloride, $[PCl_4]^+[PCl_6]^-$.

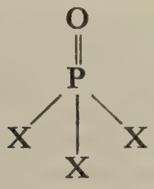
The wide-line fluorine NMR spectra of sodium, potassium, rubidium and cæsium hexafluorophosphates have been investigated from 77 to 400°K.[1113] In all cases the hexafluorophosphate ion was found to be reorientating at random about its octahedral axes above 200°K. The ease of reorientation increases with cation size and in the case of the cæsium salt the line was still narrow at 77°K. The line shapes were remarkably sensitive to physical state and, in the case of the rubidium salt, the thermal history of the samples.[1113]

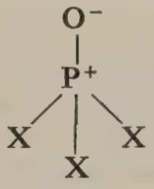
The Raman and infra-red spectra of the hexafluorophosphate ion have been reported.[260-2, 838] Potassium hexafluorophosphate shows peaks in the infra-red spectrum at 840 and 555 cm.$^{-1}$ [262, 838] A strong peak, which has been assigned[261] to the symmetrical 'breathing' frequency of the hexafluorophosphate ion, appears in the Raman spectrum of aqueous ammonium hexafluorophosphate at 741 cm.$^{-1}$ [260-1] In a melt of potassium hexafluorophosphate this band occurs at 735 cm.$^{-1}$, and other bands appear at 462 and 563 cm.$^{-1}$ [838] A P–F stretching force constant of 4·3 millidynes/A. was obtained.[838] The infra-red spectrum of the solid complex of nitryl fluoride and phosphorus pentafluoride has been interpreted[534] as indicating a structure corresponding to nitronium hexafluorophosphate, $NO_2^+.PF_6^-$. A band at 855 cm.$^{-1}$ was assigned to the hexafluorophosphate ion, in agreement with the spectrum of potassium hexafluorophosphate.

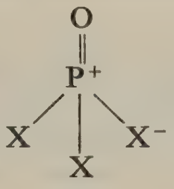
The phosphorus and fluorine nuclear magnetic resonance spectra of the hexafluorophosphate ion have been reported for the acid and the potassium salt. The phosphorus chemical shift is 118 p.p.m. (relative to 85% orthophosphoric acid),[110] the fluorine shift −5·5 p.p.m. (relative to trifluoroacetic acid), and the phosphorus–fluorine spin-spin coupling 713 c/s.[225, 634] The observed coupling pattern confirms the existence of the hexafluorophosphate ion in solution and indicates that all the fluorine atoms are equivalent and that the ion has $O_h$ symmetry. The e.s.r. spectra of $\gamma$-irradiated ammonium and potassium hexafluorophosphates have been investigated.[1113-5] The radicals $N_2H_4^+$, $PF_2$ and $PF_4$ have been identified. In the radical $PF_4$, the unpaired electron was found to cause a distortion from tetrahedral symmetry,[1114] although the average configuration at room temperature was tetrahedral, with all fluorines equivalent, because of intramolecular inversion.[1116]

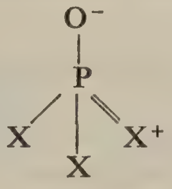
## PHOSPHORYL AND THIOPHOSPHORYL HALIDES

The nature of the P–O bond in phosphoryl compounds, as determined from physical data such as interatomic distances, dissociated energies, bond angles, dipole moments and force constants, has been discussed in some detail.[784] In most cases the structure is regarded as a resonance hybrid mainly of structures (I) and (II) below. When strongly electronegative substituents are present, the structure is thought to be mainly (I) with a small contribution from (III), while with amino and other mesomeric groups the structure may be mainly (II) with some (IV).


(I)


(II)


(III)


(IV)

The structures of most of these molecules have been determined by electron diffraction[186, 263-6]; they all have an approximately tetrahedral configuration. Structural data have also been obtained from microwave spectra.[267-9] The crystal structure of $PSBr_3$ has been determined.[270-1] The crystal is cubic with an eight-molecule cell, $a = 11{\cdot}03$ A., space group *Pa*3. Structural data for the phosphoryl and thiophosphoryl halides are summarized in Table VI. The microwave spectra have been investigated by several other workers[190, 192, 272-4, 638] and the dipole moment of $POF_3$ (1·77 ± 0·02 D) has been determined.[190]

The phosphoryl and thiophosphoryl halides have been very extensively investigated by Raman[199, 202, 210, 212, 275-85, 334, 1121, 1125, 1127] and infra-red[215, 217, 286, 664, 1120-2, 1124-30] spectroscopy as follows: phosphoryl fluoride,[215, 217, 275-6, 1124] chloride,[199, 202, 215, 275, 277-9, 664] bromide,[215, 279-80] chloride difluoride,[275-6, 1121, 1127-8] bromide difluoride,[275-6, 1121-2] fluoride dichloride,[275, 281, 1121, 1128] fluoride dibromide,[212, 275, 281, 1121-2] fluoride chloride bromide,[281] bromide dichloride,[279]

*Table VI.—Structural Data for Phosphoryl and Thiophosphoryl Halides*

| Molecule | Data (Bond distances in A.) | Reference |
|---|---|---|
| $POF_3$ | PO = 1·45 ± 0·03<br>PF = 1·52 ± 0·02<br>∠FPF = 102·5 ± 2° | 269, 267<br>(Electron diffraction and microwave spectra) |
| $PSF_3$ | PS = 1·87 ± 0·03<br>PF = 1·53 ± 0·02<br>∠FPF = 100·3 ± 2° | 269, 267<br>(Electron diffraction and microwave spectra) |
| $POCl_3$ | PO = 1·45 ± 0·03<br>PCl = 1·99 ± 0·02<br>∠ClPCl = 103·6 ± 2° | 269<br>(Electron diffraction and microwave spectra) |
|  | PO = 1·45 ± 0·05<br>PCl = $1{\cdot}99_5 \pm 0{\cdot}02$<br>∠ClPCl = 103·5 ± 1° | 263<br>(Electron diffraction) |
| $PSCl_3$ | PS = 1·85 ± 0·02<br>PCl = 2·02 ± 0·01<br>∠ClPCl = 100·5 ± 1° | 269<br>(Microwave spectra and electron diffraction) |
| $POBr_3$ | PO = 1·41 ± 0·07<br>PBr = 2·06 ± 0·03<br>∠BrPBr = 108 ± 3° | 264<br>(Electron diffraction) |
| $PSBr_3$ | PS = 1·89 ± 0·06<br>PBr = 2·13 ± 0·03<br>∠BrPBr = 106 ± 3° | 264 |
| $PSFBr_2$ | PS = 1·87 ± 0·05<br>PF = 1·50 ± 0·10<br>PBr = 2·18 ± 0·03<br>∠BrPBr = 100 ± 3° | 264 |
| $PSF_2Br$ | PS = 1·87 ± 0·04<br>PF = 1·45 ± 0·08<br>PBr = 2·14 ± 0·04<br>∠FPBr = 106 ± 3° | 264 |

chloride dibromide[279] and thiophosphoryl fluoride,[276, 1120–1, 1127, 1129] chloride,[215, 278, 282–3, 286, 334, 664, 1127] bromide,[283, 1121] chloride difluoride,[215, 276, 1121, 1127, 1130] bromide difluoride,[276, 1121, 1130] fluoride dichloride,[284, 1125–7] fluoride dibromide,[284, 1126] fluoride chloride bromide,[284] bromide dichloride,[283] and chloride dibromide.[283] The results of these investigations are consistent with the data from electron diffraction and microwave experiments; the Raman and infra-red bands are all coincident with experimental error, allowing for phase changes, as should be the case for molecules of $C_{3v}$ or lower symmetry. It has recently been pointed out[1121] that the large differences in PO stretching frequency between the liquid and gaseous state in these compounds has frequently not been taken into proper account in frequency–electronegativity relationships,[773] and also[1121] that the P=S stretching frequency is influenced more by the degree of coupling with PF and PCl stretching motions than by bond order and electronegativity considerations. The observed vibrational frequencies of these compounds are given in Table VII.

The force constants of phosphoryl fluoride,[287, 825, 848, 1123] chloride,[287–9, 848, 1123] bromide[280, 287, 289, 1123] and thiophosphoryl fluoride,[825, 1123] chloride[287, 289, 1123] and bromide[289, 825, 1123] have been calculated, and the results are given in Table VIII. An attempt has been made[828] to produce a force field applicable to $POF_3$, $POCl_3$, $PSF_3$ and $PSCl_3$ by making the assumption that analogous bonds in the different molecules have identical force constants. A fit was only obtained by using an excessive number

*Table VII.—Vibrational Spectra of Phosphoryl and Thiophosphoryl Halides*

| Compound | Frequencies quoted | Observed frequencies (cm.$^{-1}$) | References |
|---|---|---|---|
| $POF_3$ | IR (gas) | 335 ($\delta PF_3$); 473 ($\gamma_s PF_3$); 485 ($\gamma_{as} PF_3$); 875 ($p$, $\nu_s PF_3$); 990 ($\nu_{as} PF_3$); 1415 ($p$, $\nu PO$) | 217, 276, 1124 |
| $POF_2Cl$ | IR (gas) | 274 (Raman); 406, 412 ($p$); 419, 623 ($p$, $\nu PCl$); 895 ($p$, $\nu_s PF_2$); 960 ($\nu_{as} PF_2$); 1384 ($\nu_s PO$) | 276, 1121, 1128 |
| $POFCl_2$ | IR (gas) | 207 (Raman, $p$); 254 (Raman); 330 ($p$); 374, 382 ($p$); 546 ($p$, $\nu_s PCl_2$); 626 ($\nu_{as} PCl_2$); 907 ($p$, $\nu PF$); 1358 ($p$, $\nu PO$) | 276, 1121, 1128 |
| $POCl_3$ | Raman (liq.) | 193 ($\delta PCl_3$); 267·4 ($p$, $\gamma_s PCl_3$); 337·4 ($\gamma_{as} PCl_3$); 486·2 ($p$, $\nu_s PCl_3$); 581·2 ($\nu_{as} PCl_3$); 1290 ($p$, $\nu PO$) | 275 |
| $POCl_2Br$ | Raman (liq.) | 161, 172 ($p$); 242 ($p$); 285 ($p$); 327, 432 ($p$); 545 ($p$); 580, 1285 ($p$) | 279 |
| $POClBr_2$ | Raman (liq.) | 130, 157, 209·5 ($p$); 271, 291 ($p$); 391 ($p$); 492, 552 ($p$); 1275 ($p$) | 279 |
| $POBr_3$ | Raman (liq.) | 118 ($\delta PBr_3$); 173 ($p$, $\gamma_s PBr_3$); 267 ($\gamma_{as} PBr_3$); 340 ($p$, $\nu_s PBr_3$); 488 ($\nu_{as} PBr_3$); 1261 ($p$, $\nu PO$) | 275 |
| $POFBr_2$ | IR (gas) | 136 ($p$); 232, 279 ($p$); 291, 316 ($p$); 472 ($p$, $\nu_s PBr_2$); 536 ($\nu_{as} PBr_2$); 888 ($p$, $\nu PF$); 1337 ($\nu PO$) | 281, 1121–2 |
| $POF_2Br$ | IR (gas) | 243, 317 ($p$); 412, 561 ($p$, $\nu PBr$); 884 ($p$, $\nu_s PF_2$); 947 ($\nu_{as} PF_2$); 1380 ($p$, $\nu PO$) | 276, 1121–2 |
| POFClBr | Raman (liq.) | 173, 233, 298, 311, 372, 495, 590, 890, 1319 | 281 |
| $PSF_3$ | IR (gas) | 276 ($\delta PF_3$); 409 ($\gamma_{as} PF_3$); 445 ($p$, $\gamma_s PF_3$); 694 ($p$, $\nu PS$); 944 ($\nu_{as} PF_3$); 980 ($p$, $\nu_s PF_3$) | 1121, 1127 |
| $PSF_2Cl$ | IR (gas) | 198 (SPCl in-plane bend); 251 (Raman, SPCl out-of-plane bend); 317 ($\tau$, $PF_2$); 361 ($p$, $\gamma PF_2$); 395 ($p$, $\delta PF_2$); 541 ($p$, $\nu PCl$); 738 ($p$, $\nu P{=}S$); 918 ($\nu_{as} PF_2$); 946 ($p$, $\nu_s PF_2$) | 1121, 1127 |
| $PSFCl_2$ | IR (gas) | 192 ($\gamma$, $\tau PCl_2$), 268 ($p$, $\delta PCl_2$); 319 ($\gamma$SPF out-of-plane); 331 ($\gamma$SPF in-plane); 478 ($p$, $\nu_s PCl_2$); 575 ($\nu_{as} PCl_2$); 753 ($p$, $\nu P{=}S$); 912 ($p$, $\nu PF$) | 1127 |
| $PSCl_3$ | IR (gas) | 174 (Raman, $\delta PCl_3$); 248 ($\gamma_{as} PCl_3$); 252 ($\gamma_s PCl_3$); 431 ($p$, $\nu_s PCl_3$); 547 ($\nu_{as} PCl_3$); 770 ($p$, $\nu P{=}S$) | 1127 |
| $PSCl_2Br$ | Raman (liq.) | 150, 206 ($p$); 230, 371 ($p$); 493 ($p$); 536, 743 ($p$) | 283 |
| $PSClBr_2$ | Raman (liq.) | 121 ($p$); 136, 190, 196 ($p$); 205, 333 ($p$); 436, 500 ($p$); 729 ($p$) | 283 |
| $PSBr_3$ | IR (gas) | 133 ($\gamma_{as} PBr_3$); 165 ($p$, $\gamma_s PBr_3$); 175 ($\delta$SPBr); 299 ($p$, $\nu_s PBr_3$); 438 ($\nu_{as} PBr_3$); 726 ($p$, $\nu P{=}S$) | 283, 1121 |

of constants.[829] Values of bond dipole moments,[848] and their derivatives, have been proposed for $POCl_3$.

*Table VII.—continued)*

| Compound | Frequencies quoted | Observed frequencies (cm.$^{-1}$) | References |
|---|---|---|---|
| $PSFBr_2$ | IR (gas) | 129, 162, 218 ($p$); 254, 274 ($p$); 381 ($p$); 483, 732($p$); 900 ($p$) | 284, 1126 |
| $PSF_2Br$ | IR (gas) | 175 (Raman); 231 (Raman); 288 (Raman, $p$); 298 (Raman); 389 ($p$, $\gamma_s PF_2$); 477 ($p$, $\nu PBr$); 719 ($p$, $\nu P{=}S$); 911 ($\nu_{as} PF_2$); 938 ($\nu_s PF_2$) | 276, 1121, 1130 |
| PSFClBr | Raman (liq.) | 160, 175, 245, 267, 314, 414, 535, 729, 892 | 284 |

*Table VIII.—Force Constants of Phosphoryl and Thiophosphoryl Halides (Valence Force Fields)*

| Compound | $F_{P-O}$ millidynes/A. | $F_{P-X}$ millidynes/A. | Reference |
|---|---|---|---|
| $POF_3$ | 10·95 | 6·31 | 848 |
| | 11·39 | 6·18 | 287 |
| | 11·00 | 4·72 | 825 |
| | 10·72 | 4·62 | 1123 |
| $POCl_3$ | 9·98 | 2·45 | 287 |
| | 9·6 | 2·87 | 288 |
| | 10·97 | 3·08 | 289 |
| | 10·38 | 2·56 | 848 |
| | 10·54 | 3·01 | 1123 |
| $POBr_3$ | 9·59 | 2·11 | 287 |
| | 10·32 | 2·36 | 289 |
| | 10·32 | 2·09 | 1123 |
| $PSF_3$ | 4·50 | 4·77 | 825 |
| | 5·01 | 4·75 | 1123 |
| $PSCl_3$ | 4·14 | 2·49 | 287 |
| | 5·60 | 2·50 | 289 |
| | 4·95 | 2·13 | 1123 |
| $PSBr_3$ | 5·37 | 1·94 | 289 |
| | 4·25 | 1·88 | 825 |
| | 4·89 | 1·97 | 1123 |

The Verdet constant of phosphoryl chloride at 5780 A. is $2{\cdot}18 \times 10^{-2}$.[198] The ultraviolet spectrum of phosphoryl chloride has been reported[194, 1017] as showing a broad maximum around 196–185 mμ.[1017]

The nuclear magnetic resonance spectra of phosphoryl fluoride,[225, 832] chloride,[110, 171, 226, 290, 612, 833] bromide,[226, 612, 833] fluoride dichloride, chloride difluoride,[110, 225, 290–1] fluoride dibromide, bromide difluoride,[1122] bromide dichloride and chloride dibromide,[833] thiophosphoryl fluoride,[1131] chloride difluoride,[1131] bromide difluoride,[1131] chloride,[226, 612, 833] bromide,[226, 833] chloride dibromide and bromide dichloride[833] have been examined. Phosphorus chemical shifts (relative to 85% orthophosphoric acid) are as follow:

| Compound | Chemical shift p.p.m. | Reference |
|---|---|---|
| $POF_3$ | 35·5 | 832 |
| $POF_2Cl$ | 14·8 | 110 |
| $POFCl_2$ | 0·0 | 110 |
| $POF_2Br$ | 28·1 | 1122 |
| $POFBr_2$ | 111·3 | 1122 |
| $POCl_3$ | −2·2 | 833 |
|  | −1·9 | 226, 612 |
|  | −5·4 | 110 |
| $POCl_2Br$ | 29·6 | 833 |
| $POClBr_2$ | 64·8 | 833 |
| $POBr_3$ | 102·9 | 226, 612 |
|  | 103·4 | 833 |
| $PSF_3$ | −32·4 | 1131 |
| $PSF_2Cl$ | −50·0 | 1131 |
| $PSFCl_2$ | −43·0 | 1339 |
| $PSF_2Br$ | −28·6 | 1131 |
| $PSFBr_2$ | +17·2 | 1339 |
| $PSCl_3$ | −28·8 | 226, 612, 833 |
|  | −30·8 | 110 |
| $PSCl_2Br$ | 14·5 | 833 |
| $PSClBr_2$ | 61·4 | 833 |
| $PSBr_3$ | 111·8 | 226, 833 |

Fluorine chemical shifts and phosphorus–fluorine spin-spin coupling constants $J_{P-F}$ are as follow:

| Compound | Chemical shift p.p.m. | $J_{P-F}$ cycles/sec. | Reference |
|---|---|---|---|
| $POF_3$ | +15·8(a) | 1055 | 225 |
|  |  | 1080 | 832 |
| $POClF_2$ | −30·4(a) | 1128 | 225 |
| $POCl_2F$ | −69·0(a) | 1171 | 225 |
| $PSF_3$ | −32·4(b) | 1180–4 | 1131 |
| $PSF_2Cl$ | +15·9(b) | 1218–20 | 1131 |
| $PSFCl_2$ | −15·6(b) | 1240–48 | 1339 |
| $PSF_2Br$ | +2·3 | 1249–52 | 1131 |
| $PSFBr_2$ | −31·3 | 1269–75 | 1339 |

(a) Relative to trifluoroacetic acid.
(b) Relative to fluorotrichloromethane.

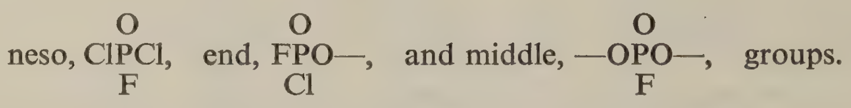
The chlorine nuclear quadrupole resonance of phosphoryl chloride (at 77°K.) and fluoride dichloride (at 20°K.) have been investigated.[228] In both cases two lines per chlorine isotope were observed, indicating two non-equivalent chlorine positions in the lattice.

The infra-red and $^1H$ and $^{19}F$ NMR spectra of hydrothiophosphoryl difluoride, $SPF_2H$, have been reported.[1135] The low $\tau$-value (1·93) of the proton resonance and the large phosphorus–proton spin-spin coupling (725 c/s), as well as the presence of PH stretching and bending vibrations and a P=S stretching vibration at 2458, 1016 and 705 $cm.^{-1}$ in the infra-red spectrum, support the proposed structure based on quinquevalent phosphorus. The fluorine chemical shift is +46·1 p.p.m. relative to $CCl_3F$ and the remaining coupling constants are $J_{PF} = 1153·3$ c/s, $J_{PH} = 99·0$ c/s.

## PYROPHOSPHORYL HALIDES AND RELATED COMPOUNDS

The Raman and $^{19}F$ NMR spectra of pyrophosphoryl fluoride, $P_2O_3F_4$, have been investigated.[901] The NMR spectrum shows a simple doublet, suggesting a symmetrical structure. The Raman spectrum shows 19 lines assignable to fundamentals, and some are depolarized, indicating symmetry in the molecule. The spectra are therefore consistent with the structure $F_2(O)POP(O)F_2$.

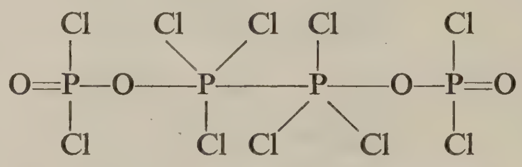
The infra-red[902] and $^{31}P$ NMR[1136–7] spectra of pyrophosphoryl dichloride difluoride, $P_2O_3Cl_2F_2$, have been reported.[1136] A symmetrical doublet (chemical shift +19 p.p.m. relative to 85% $H_3PO_4$ [1136]) indicates that the molecule has the symmetrical structure ClF(O)POP(O)ClF. The spectrum has been analysed as an $A_2X_2$ system[1137] with the following parameters $J_{P_1F_1}=J_{P_2F_2}=1121$ c/s, $J_{P_1P_2}=21$ c/s, $J_{P_1F_2}=J_{P_2F_1}=2$ c/s $>J_{F_1F_2}\geqslant 0$, with the sign of $J_{P_1F_1}$ opposite to that of $J_{P_1F_2}$. An NMR study[1137] has shown that this compound slowly reorganizes at 50°C. to a combination of



$$\text{neso, } \mathrm{Cl\underset{F}{\overset{O}{P}}Cl},\quad \text{end, } \mathrm{F\underset{Cl}{\overset{O}{P}}O}\text{—},\quad \text{and middle, } \text{—}\mathrm{O\underset{F}{\overset{O}{P}}O}\text{—},\quad \text{groups.}$$

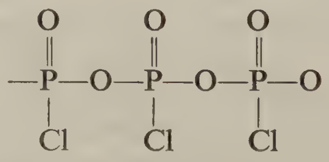
NMR parameters of these groups are as follows (relative to trifluoroacetic acid and 85% $H_3PO_4$): neso, $\delta_F=-70{\cdot}2$, $\delta_P=-0{\cdot}8$, $J_{PF}=1179$ c/s; end, $\delta_F=-41{\cdot}0$, $\delta_P=+19{\cdot}0$, $J_{PF}=1121$ c/s; middle, $\delta_F=-9{\cdot}8$, $\delta_P=+44{\cdot}0$, $J_{PF}=1050$ c/s.

The infra-red and Raman spectra of pyrophosphoryl chloride, $P_2O_3Cl_4$, have been determined.[292, 336] The Raman spectrum[336] showed 18–19 lines, with a single polarized phosphoryl band at 1312 cm.$^{-1}$, indicating that the phosphoryl groups are very weakly coupled and must be on different phosphorus atoms. A number of depolarized lines indicated that the molecule had some symmetry. The structure is evidently $Cl_2(O)POP(O)Cl_2$. Recent work[901] on the infra-red spectrum led to some reassignment of the earlier data. The Raman and infra-red spectra of a compound[292, 335, 337, 937–8] having the empirical formula $P_4O_4Cl_{10}$ have been investigated.[292] Infra-red absorption attributed to P=O, P–O–P, and P–Cl linkages led to the suggestion that the compound was sym-bis(dichlorophosphato)hexachlorodiphosphorane,



The phosphorus nuclear magnetic resonance spectrum was also reported as indicating a symmetrical ABBA type of structure. Recent work, however,[933] suggests that the compound is in fact $P_2NOCl_5$ (see page 506).

In a nuclear magnetic resonance investigation[837] of a series of polyphosphoryl chlorides over a range of composition, $^{31}P$ resonance peaks at $+50\pm 3$, +28–32, +7–11 p.p.m. (relative to 85% orthophosphoric acid) were assigned to branching, middle and end groups of the form $(O\frac{1}{2})_3PO$, $(O\frac{1}{2})_2P(O)Cl$ and $O\frac{1}{2}P(O)Cl_2$ respectively, where $(O\frac{1}{2})$ denotes an oxygen atom shared with an adjacent phosphorus atom. Pyrophosphoryl chloride itself was found to have a chemical shift of 9·9 p.p.m. The infra-red spectrum of a polyphosphoryl chloride of composition $PO_2Cl$ has been interpreted in terms of a structure[1134]:



$$-\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{O}-\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{O}-\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{O}$$

The infra-red and $^{31}P$ NMR spectra of a compound described as $P_2S_2I_4$ were interpreted[1138] as indicating the structure $I_2(S)PP(S)I_2$. Bands were assigned to

P=S and $PI_2$ stretching at 725 and 329 (antisym.) and 301 (sym.) cm.$^{-1}$ respectively, and the NMR spectrum shows a singlet peak at $-106$ p.p.m. relative to 85% $H_3PO_4$.

## Adducts of Phosphoryl Halides

The interaction of phosphoryl chloride with various acceptor molecules has been investigated by infra-red and Raman spectroscopy.[293-4] The decrease in frequency of the phosphoryl vibration has been correlated with the interaction of the donor function of the oxygen with different acceptor molecules. The interaction of phosphorus oxychloride with arsenic trichloride or antimony trichloride is considered to be dipolar, while that with stannic chloride or antimony pentachloride leads to adduct formation by an acceptor-donor mechanism.[294] A Raman-effect study of the phosphoryl chloride–bismuth trichloride system[654] suggested that it is of a similar type to the complexes with arsenic and antimony trichlorides. The crystal structure of the phosphoryl chloride–stannic chloride adduct, $2POCl_3,SnCl_4$ [295] shows that both phosphoryl chloride molecules are bonded in the same way to the stannic chloride, discounting an earlier suggestion[293] that one is free.

The structures of the phosphoryl chloride–aluminium trichloride and phosphoryl chloride–gallium trichloride adducts have been investigated by Raman and infra-red spectroscopy.[296] The alternatives considered were a dissociated structure, an ionic structure of the type $POCl_2^+.AlCl_4^-$, and a co-ordinated structure of the type $Cl_3POAlCl_3$. It was concluded that the co-ordinated type of structure was probably correct.

Raman spectroscopic investigations of the phosphoryl chloride–antimony pentachloride system[293-4, 297, 655] suggested that the structure was ionic, with oxydichlorophosphonium, $POCl_2^+$, ions and hexachloroantimonate, $SbCl_6^-$, ions in both liquid and solid. This suggestion has been confirmed for the liquid by potentiometric measurements,[298] but has been disproved for the solid by the crystal structure determination[299, 300, 1140] which shows a co-ordinated structure with no transfer of a chlorine ion. The structure is orthorhombic with a four-molecule cell, $a=8{\cdot}06$, $b=16{\cdot}42$, $c=8{\cdot}93$ A. The space group is *Pnmb* and bond lengths are P–O = 1·52 A., Sb–O = 2·11 A.; the angle POSb = 146·5°. The adducts of tantalum and niobium pentachlorides with phosphoryl chloride are isostructural with that above, having $a=8{\cdot}1$, $b=16{\cdot}4$, $c=9{\cdot}0$ A.[1141] and $a=8{\cdot}07$, $b=16{\cdot}23$, $c=8{\cdot}83$ A. respectively.[1142]

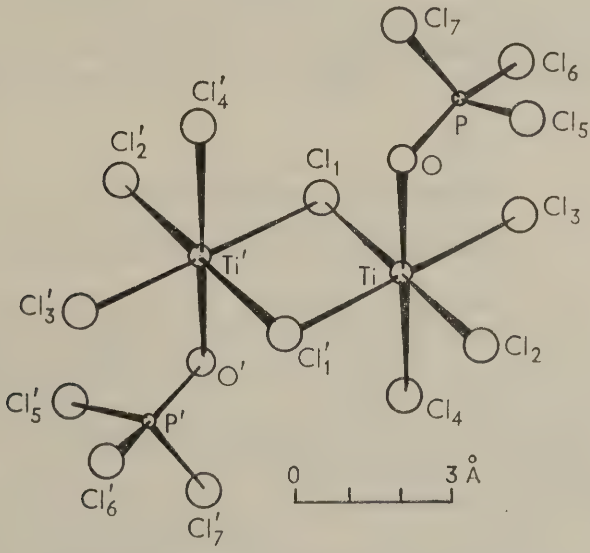


FIG. 3.—The molecule of the addition compound $(TiCl_4,POCl_3)_2$

The infra-red spectra of adducts of phosphoryl chloride with boron trifluoride and boron trichloride have been reported[259] and suggest co-ordination structures $Cl_3PO \rightarrow BF_3$ and $Cl_3PO \rightarrow BCl_3$.

Infra-red and Raman spectra of a series of adducts of phosphoryl chloride and bromide with boron trichloride and tribromide, aluminium trichloride and tribromide, and gallium, indium, and thallium trichlorides[1139] were interpreted as indicating co-ordination through the oxygen atoms, from the observed reductions in PO stretching frequency.

The crystal structure of the adduct of titanium tetrachloride and phosphorus oxychloride, $(TiCl_4,POCl_3)_2$, has been determined.[653] The structure is orthorhombic, with $a = 12{\cdot}42$, $b = 12{\cdot}76$, $c = 13{\cdot}51$ A., space group *Pbca*. Two monoclinic modifications, with cell dimensions $a = 9{\cdot}9$, $b = 8{\cdot}7$, $c = 12{\cdot}3$ A., $\beta = 98°$, and $a = 13{\cdot}9$, $b = 12{\cdot}1$, $c = 19{\cdot}1$ A., $\beta = 105°$, were also reported. The orthorhombic structure is built up of dimeric molecules $(TiCl_4,POCl_3)_2$ with double chlorine bridges between the two titanium atoms of the dimer (Fig. 3). The co-ordination around the titanium atoms is octahedral, with the oxygen of the phosphoryl chloride acting as donor. The approximately tetrahedral configuration of the phosphoryl chloride is preserved. Bond lengths are P–O 1·44, Ti–O, 2·10, P–Cl 1·96 (av.), Ti–Cl 2·20–2·54 A., and the angle P–O–Ti = 152°.

The crystal structure of the adduct of tin tetrachloride with two moles of phosphoryl chloride, $SnCl_4,2POCl_3$, has been determined.[1143] The structure is orthorhombic, space group *Pnnm*, with $a = 14{\cdot}53$, $b = 14{\cdot}24$, $c = 8{\cdot}02$ A. The structure contains discrete molecules of $SnCl_4,2POCl_3$ in which the tin atom is octahedrally co-ordinated to the four chlorines and two $OPCl_3$ groups which are *cis*- to each other. The $OPCl_3$ groups are crystallographically non-equivalent, but preserve their tetrahedral form. Bond lengths are: Sn–O, 2·30, 2·25; P–O, 1·41, 1·49; PCl 1·96 (av.) A., and the Sn–O–P angles are 144° and 151°. The adduct $TiCl_4,2POCl_3$ is isostructural with $SnCl_4,2POCl_3$.[1141]

The chlorine nuclear quadrupole resonance spectra of the adducts $SbCl_5,POCl_3$, $SnCl_4POCl_3$ and $(TiCl_4,POCl_3)_2$ have been reported.[1144] Signals were assigned on the basis of the crystal structures. The temperature dependence of the spectra suggested that the $PCl_3$ groups were capable of restricted rotation.

The infra-red spectra of adducts of pyrophosphoryl chloride with antimony pentachloride and tin tetrachloride, $2SbCl_5,P_2O_3Cl_4$, and $SnCl_4,P_2O_3Cl_4$, have been reported.[1145]

## OXIDES OF PHOSPHORUS

### Phosphorus Pentoxide, $P_4O_{10}$

The structure of the phosphorus pentoxide molecule has been determined by electron diffraction.[303–4, 378, 1150] The cage-like structure (Fig. 4) has four phosphorus atoms, each carrying an oxygen atom, at the corner of the cage. Each phosphorus is bonded to two of the six oxygens which lie in the walls of the cage. Recent electron diffraction work[1150] has led to more accurate data, as follows: PO $1{\cdot}604 \pm 0{\cdot}003$ A., PO (apical) $1{\cdot}429 \pm 0{\cdot}004$ A., POP $123{\cdot}5 \pm 0{\cdot}7°$.

The condensed phases of phosphorus pentoxide include at least three crystalline forms, glasses and two liquid forms.[305–7] The *H* (hexagonal) form[308] consists of discrete $P_4O_{10}$ molecules having the same form as those in the gaseous state, and similar dimensions. The rhombohedral unit cell has $a = 7{\cdot}43$ A., $\alpha = 87°$, contains two molecules of $P_4O_{10}$, and the space group is $R3_c$. This structure has recently been refined,[744] resulting in bond lengths of $1{\cdot}60 \pm 0{\cdot}02$ A. for P–O (internal) and $1{\cdot}40 \pm 0{\cdot}02$ A. for P–O (apical), with a P–O–P angle of $124\frac{1}{2}°$. The polymeric *O* (orthorhombic) form of phosphorus pentoxide has a cell[309] with $a = 16{\cdot}3$ A., $b = 8{\cdot}12$ A., $c = 5{\cdot}25$ A., containing eight molecules, with space group *Fdd*2. The structure[309] consists of infinite sheets of linked $PO_4$ tetrahedra which form a series of interlocking rings (Fig. 5). There are no discrete molecules.

The stable, *O′*, form of $P_4O_{10}$ [310] also has a polymeric structure. The orthorhombic

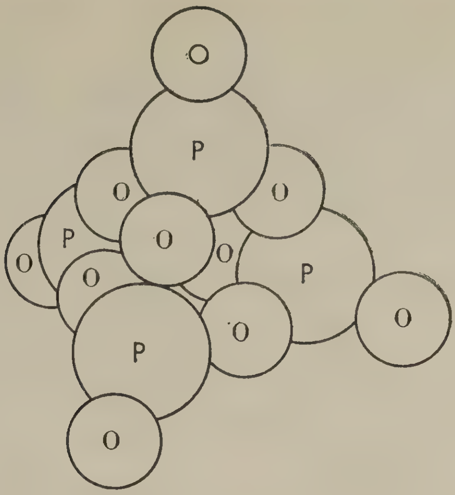


FIG. 4.—The structure of $P_4O_{10}$

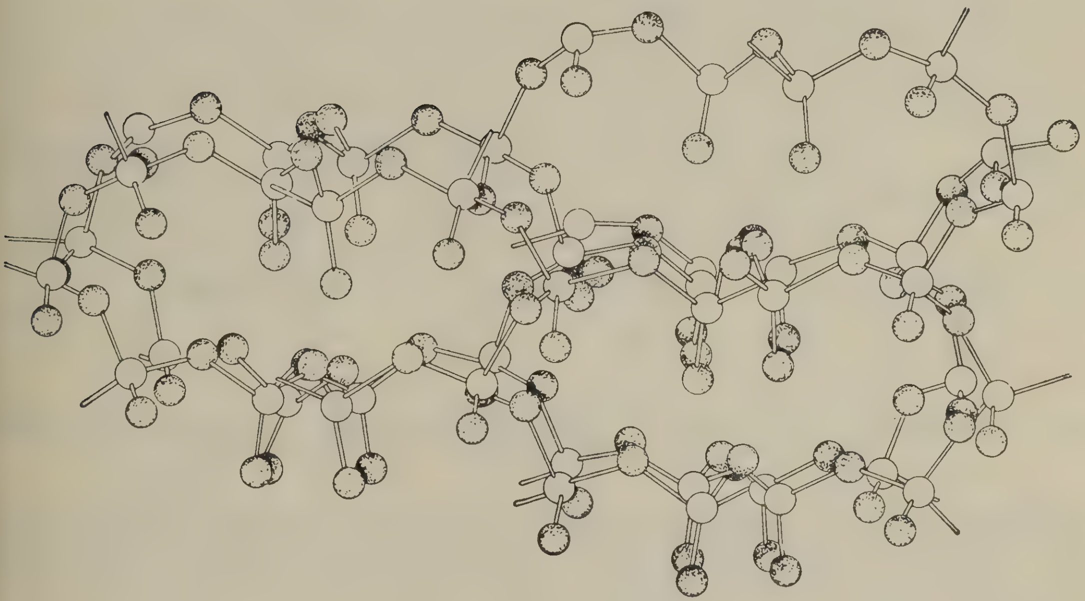


FIG. 5.—Structure of the *O*-form of phosphorus pentoxide. The white balls represent phosphorus atoms and the shaded balls oxygen atoms

unit cell contains 4 molecules of $P_2O_5$ and has $a=9{\cdot}23$ A., $b=7{\cdot}18$ A., $c=4{\cdot}94$ A. The space group is *Pnam*. In this form of $P_2O_5$ the $PO_4$ tetrahedra form a system of corrugated sheets (Fig. 6).

When the *H* form is melted, a limpid mobile liquid is obtained, presumably composed of $P_4O_{10}$ molecules. When the other forms are melted a viscous liquid is obtained, probably with a polymeric structure. The limpid liquid eventually polymerizes to give the more viscous form.[307]

The Raman[319] and infra-red[215, 322, 664] spectra of the *H* form of phosphorus pentoxide have been determined. The spectra may be satisfactorily assigned on the basis of $T_d$ molecular symmetry, in agreement with the *X*-ray structure. The symmetric ($A_1$) apical P=O breathing frequency was assigned at 1417 cm.$^{-1}$ and the other $A_1$ frequencies were assigned at 721 and either 424 or[1151] 559 cm.$^{-1}$ Strong infra-red bands at 1390, 1015, 764 and 573 or[1151] 424 cm.$^{-1}$, were assigned to $F_2$ vibrations, and the other $F_2$ vibrations to Raman bands at 329 and 257 or[1151] 278 cm.$^{-1}$ *E* vibrations were assigned at 952, 650 or[1151] 329, and 278 or[1151] 257 cm.$^{-1}$ [319, 322] Force constants have been estimated,[320, 1151] and values of $F_{PO}$ (bridge) $= 3{\cdot}9$

and $F_{PO}$ (apical) = 10·84 millidynes/A. proposed.[1151] Recent work[1152] on the infra-red and Raman spectra has led to some revision of the earlier assignments. The infra-red spectrum was obtained as far as 200 cm.$^{-1}$ and showed the three lowest $F_2$ fundamentals to be 573, 424 and 278 cm.$^{-1}$ Weak lines at 650 and 329 cm.$^{-1}$ in the Raman spectrum were not confirmed. The Raman counterpart of the infra-red band at 573 was observed separately from the strong band at 556, indicating that the latter was the remaining $A_1'$ fundamental. The band at 257 cm.$^{-1}$ is clearly an $E''$ fundamental but the assignment of the others remains uncertain. Force constants have been calculated as follows: $F_{PO}$ (bridge) 5·26, $F_{P=O}$ (apical) 10·95 millidynes A.[1152] Phosphorus pentoxide shows no ultra-violet absorption as far as 2100 A.,[311] and complete absorption beyond 2200 A.[194]

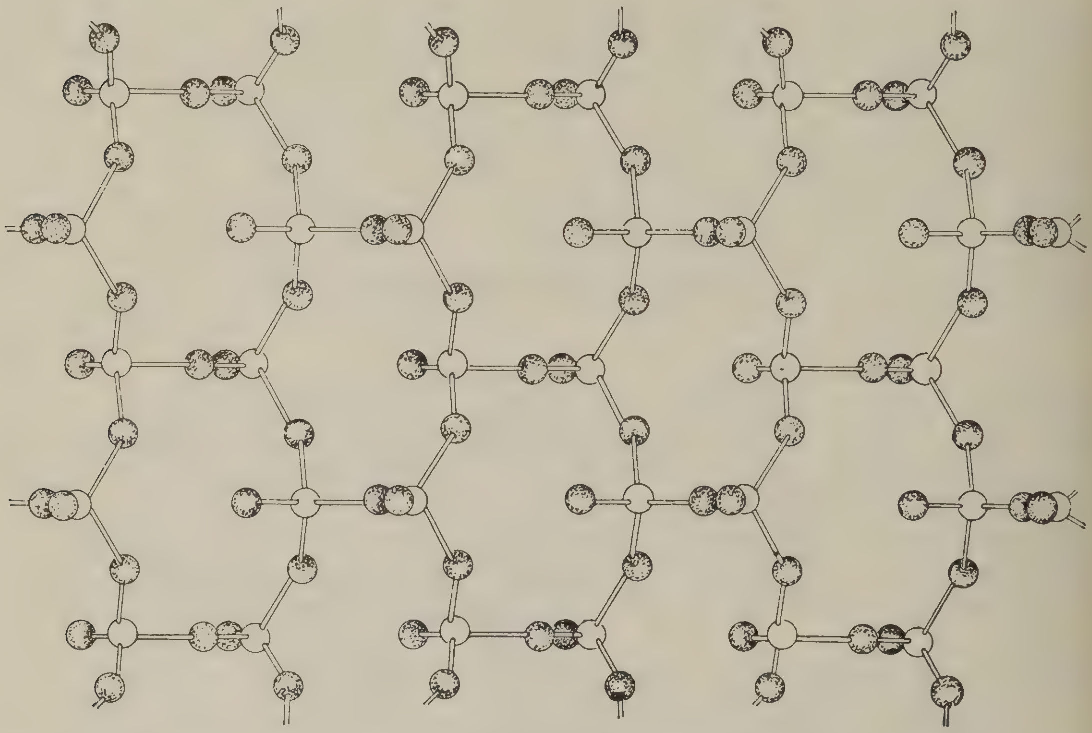


FIG. 6.—Structure of the *O′*-form of phosphorus pentoxide. The white balls represent phosphorus atoms and the shaded balls oxygen atoms

## Phosphorus Trioxide, $P_4O_6$

The structure of the phosphorus trioxide molecule has been determined by electron diffraction.[303-4] The molecule is cage-like, similar to that of phosphorus pentoxide with the four apical oxygens removed (Fig. 7). These results confirm those of early

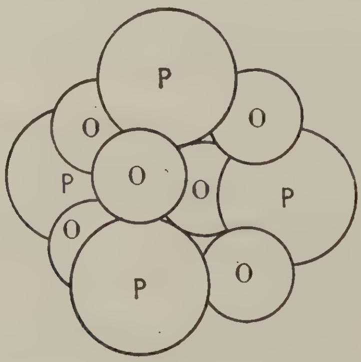


FIG. 7.—The structure of $P_4O_6$

molecular weight determinations.[313] The P–O bond length is 1·65±0·02 A., and the angles, P–O–P = 127·5±1°, O–P–O = 99±1°. The Raman[314–6] and infra-red[542] spectra have been determined, and assigned on the basis of $T_d$ symmetry, in agreement with electron diffraction results. The two totally symmetric ($A_1$) vibrations were thought[314, 1151] to be accidentally degenerate at 613 cm.$^{-1}$ $F_2$-type vibrations were assigned to strong infra-red bands, which also appear in the Raman spectrum, at 911 and 636 cm.$^{-1}$ and to Raman bands at 302 and 407 cm.$^{-1}$ $E$-type modes were assigned to Raman bands at 1029 and 465 cm.$^{-1}$ [314, 542] or 723 and 302 cm.$^{-1}$ [1151] The P–O stretching force constant has been estimated at 4·75 [320] or 3·8[1151] millidynes/A. These results refer to the Raman spectrum of the liquid and the infra-red spectrum of the solid; an incomplete Raman spectrum of the solid[314] is similar to that of the liquid, and it is clear that the solid contains discrete $P_4O_6$ molecules. A different polymorph of solid phosphorus trioxide has, however, been prepared,[315] possibly having a polymeric structure analogous to the orthorhombic forms of phosphorus pentoxide.

Recent work[1153] has led to some revision of these assignments. Far infra-red spectra (to 200 cm.$^{-1}$) confirm the assignment of the $F_2$ fundamentals at 919, 643, 402 and 302 cm.$^{-1}$ A second polarized Raman band at 563 cm.$^{-1}$ was assigned to the second $A_1$ fundamental, which is not therefore coincident with 613 cm.$^{-1}$ The lines previously reported at 370 and 465 cm.$^{-1}$ were found to be due to dissolved phosphorus and the band at 1029 cm.$^{-1}$ was not confirmed. Proposed assignments for the two $E$ modes were 691 and 285 cm.$^{-1}$ Force constants were calculated, the value for the PO valence stretching constant being 3·41.[1153]

The $^{31}P$ NMR spectrum of $P_4O_6$ [1154] gives a single very sharp peak, and its use as a standard for referencing $^{31}P$ NMR spectra has been proposed.[1154] The chemical shift from 85% orthophosphoric acid is −112·5±0·1 p.p.m.[1154]

NMR spectra of a number of addition compounds of $P_4O_6$ have been reported, as follows:

| Compound | Chemical shifts | | H | $J_{POP}$ | Reference |
|---|---|---|---|---|---|
| | co-ord. P[(a)] | unco-ord. P[(a)] | | c/s | |
| $P_4O_6,BH_3$ | −90·4 | −118·2 | 9·3τ | 27·5 | 1155 |
| $P_4O_6,2BH_3$ | −98·7 | −119·2 | 9·35 | 24·7 | 1155–6 |
| $P_4O_6,3BH_3$ | −103·6 | −114·6 | — | 21 | 1155 |

[(a)] p.p.m. relative to 85% $H_3PO_4$.

The ultra-violet absorption spectrum of phosphorus trioxide has been determined[311]; there is continuous absorption, possibly due to solid phosphorus pentoxide, in the visible region, as well as two-band systems which have been partly analysed.

### 'Phosphorus Tetroxide', $(PO_2)_n$

Vapour density measurements on this oxide[317] indicated molecular weights in the range 293–721, suggesting a cage-like molecule larger than that of phosphorus pentoxide.[318] The electron diffraction pattern has been reported[303] to be almost identical with that of phosphorus pentoxide.

Recent work[1157] has shown that there are two phases around this composition, and the crystal structures of these phases have been determined.[1158–9] The α-phase,[1157] consisting of $P_4O_9$ molecules, can accept up to 90% of $P_4O_8$ molecules without change in structure. The β-phase of $P_4O_8$ molecules can similarly accept considerable substitution of $P_4O_7$ molecules.

The structure[1158] of $P_4O_9$ is rhombohedral, with $a = 10{\cdot}05$ A. and $\alpha = 57{\cdot}0°$, space group $R\bar{3}c$. The alternative monoclinic cell has $a = 9{\cdot}66$, $b = 10{\cdot}05$, $c = 13{\cdot}90$ A., $\alpha = 93{\cdot}0°$. The $P_4O_9$ resembles a molecule of $P_4O_{10}$ with one apical oxygen removed. This structure has recently been refined[1150] and more accurate bond lengths obtained. The molecular dimensions, which resemble those of $P_4O_{10}$ for the $P_V$ part of the molecule and $P_4O_6$ for the $P_{III}$ part, are as follows: PO apical $1{\cdot}418 \pm 0{\cdot}014$, $P_V$–O–($P_{III}$) $1{\cdot}605 \pm 0{\cdot}017$, $P_{III}$–O $1{\cdot}661 \pm 0{\cdot}013$, $P_V$–O–($P_V$) $1{\cdot}590 \pm 0{\cdot}012$ A., $P_VOP_V$ $122{\cdot}8 \pm 0{\cdot}7$, $P_V$–O–$P_{III}$ $114{\cdot}3/114{\cdot}9 \pm 0{\cdot}8$, $OP_{III}O$ $96{\cdot}7 \pm 0{\cdot}7$, $(P_V)OP_VO(P_{III})$ $102{\cdot}5/103{\cdot}1 \pm 0{\cdot}8$, $(P_V)OP_VO(P_V)$ $100{\cdot}9 \pm 0{\cdot}8°$.

The structure[1159] of $P_4O_8$ is monoclinic with $a = 9{\cdot}66$, $b = 10{\cdot}10$, $c = 6{\cdot}93$ A., $\beta = 96{\cdot}8°$, $Z = 4$, space group $C2/c$. The $P_4O_8$ and $P_4O_7$ molecules resemble $P_4O_{10}$ molecules with two or three apical oxygens removed. Molecular dimensions are: P=O 1·40, $P_V$–O–($P_V$) 1·60, $P_V$–O–($P_{III}$) 1·58, $P_{III}$–O–($P_V$) 1·65, $P_{III}$–O–($P_{III}$) 1·61 A., $P_VOP_V$ 122°, $P_VOP_{III}$ 124/126°, $P_{III}OP_{III}$ 132°.

$P_4O_9$ molecules have been reported to be in vapour equilibrium with $P_4O_{10}$ in a mass-spectrometric study[1160] of commercial phosphorus pentoxide.

### Phosphorus Suboxides

There is little structural information on these products, which are amorphous materials of variable composition. A compound of composition $P_4O$ has been investigated[953] by *X*-ray methods and the radial distribution function for the phosphorus atoms determined. A structure was proposed, in agreement with the radial distribution function, in which the phosphorus atoms are linked into sheets of 6-membered non-planar fused rings. These sheets are stacked together in a staggered configuration giving two types of distorted cubic polyhedra (shown schematically in the figure), each having six edges of P–P bonds and six of Van der Waals contacts. The first type consists of a non-planar six-membered ring with Van der Waals contacts to single phosphorus atoms in sheets above and below. The second type consists of two network points ($P_4$ groups) in adjacent sheets, linked by Van der Waals contacts. The second type of polyhedron is said to be bigger and to be the preferred oxygen site.

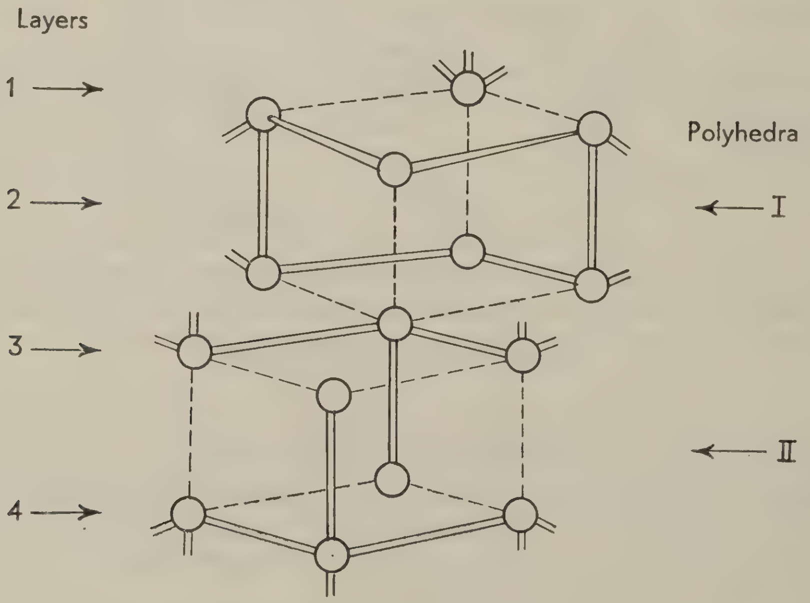


FIG. 8.—Arrangement of phosphorus atoms in $P_4O$

## PHOSPHORUS SULPHIDES

The crystal structure of the crystalline form of tetraphosphorus decasulphide, $P_4S_{10}$, has been determined.[323] The molecular structure (Fig. 9) is similar to that of phosphorus pentoxide. Molecular parameters from a recent[1163] refinement of the structure are: P–S (cage) $2{\cdot}097 \pm 0{\cdot}015$ A., P–S (apical) $1{\cdot}908 \pm 0{\cdot}015$ A., PSP = 109·8°, S=P–S = 109·6°, S–P–S = 109·3°. The crystal is triclinic, with a two-molecule cell having[1163] $a=9{\cdot}072\pm0{\cdot}003$, $b=9{\cdot}199\pm0{\cdot}003$, $c=9{\cdot}236\pm0{\cdot}003$ A., $\alpha=92{\cdot}58\pm0{\cdot}07°$, $\beta=100{\cdot}90\pm0{\cdot}1°$, $\gamma=110{\cdot}18\pm0{\cdot}07°$. The space group is $P\bar{1}$. The $^{31}$P NMR spectrum of the rapidly rotating solid[971] shows a single peak at $-45$ p.p.m. relative to 85% $H_3PO_4$.

The crystal structure of phosphorus heptasulphide, $P_4S_7$, has also been determined[323, 324] and recently refined.[1163] The molecule has an unusual cage structure with two triply bonded and two quadruply bonded phosphorus atoms (Fig. 9). The molecular symmetry approximates to $C_{2v}$. The bond lengths (all $\pm0{\cdot}007$ A., see Fig. 9) are:

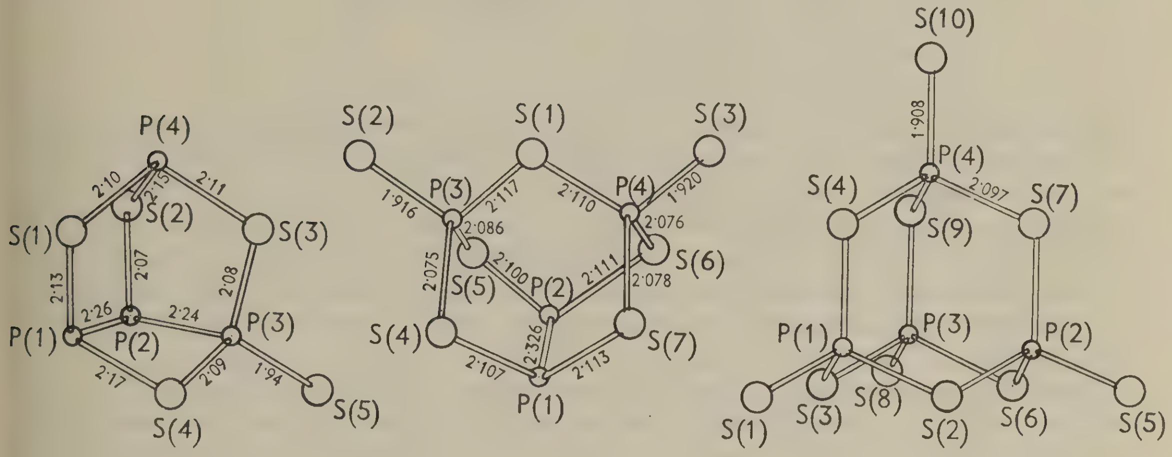


FIG. 9.—From left to right: molecules of $P_4S_5$, $P_4S_7$ and $P_4S_{10}$ with bond lengths in A. For $P_4S_{10}$ average values are given for bonds which are equivalent for the assumed $\bar{4}3\,m$ symmetry

| | A. | | A. |
|---|---|---|---|
| $P_1P_2$ | 2·326 | $P_3S_4$ | 2·075 |
| $P_1S_4$ | 2·107 | $P_3S_5$ | 2·086 |
| $P_2S_5$ | 2·100 | $P_4S_1$ | 2·110 |
| $P_2S_6$ | 2·111 | $P_4S_3$ | 1·920 |
| $P_3S_1$ | 2·117 | $P_4S_6$ | 2·076 |
| $P_3S_2$ | 1·916 | $P_4S_7$ | 2·078 |

Angles ($\pm0{\cdot}7°$, averaged as for $C_{2v}$ symmetry, see Fig. 9) are:

| | | | |
|---|---|---|---|
| $S_2P_3S_1$ | 107·7° | $S_4P_3S_5$ | 102·8° |
| $P_3S_1P_4$ | 110·1° | $P_3S_4P_1$ | 102·4° |
| $S_2P_3S_4$ | 114·0° | $S_4P_1P_2$ | 102·7° |
| $S_4P_3S_1$ | 109·1° | $S_4P_1S_7$ | 103·9° |

The crystal is monoclinic, space group $P2_1/n$, with a four-molecule cell of $a=8{\cdot}895\pm0{\cdot}004$, $b=17{\cdot}44\pm0{\cdot}015$, $c=6{\cdot}779\pm0{\cdot}004$, $\beta=92{\cdot}73\pm0{\cdot}1°$.

Tetraphosphorus pentasulphide, $P_4S_5$,[325] has an even more curious structure than that of $P_4S_7$. It is completely unsymmetrical (Fig. 9).

The molecular parameters from the later refinement[1163] are as follows (see Fig. 9, bond lengths $\pm0{\cdot}015$ A., angles $\pm0{\cdot}7°$):

| | | | |
|---|---|---|---|
| $P_1P_2$ | 2·26 A. | $P_3S_4$ | 2·09 A. |
| $P_1S_1$ | 2·13 A. | $P_3S_5$ | 1·94 A. |
| $P_1S_4$ | 2·17 A. | $P_4S_1$ | 2·10 A. |
| $P_2P_3$ | 2·24 A. | $P_4S_2$ | 2·15 A. |
| $P_2S_2$ | 2·07 A. | $P_4S_3$ | 2·11 A. |
| $P_3S_3$ | 2·08 A. | | |

| | | | |
|---|---|---|---|
| $S_1P_4S_2$ | 100·3° | $S_3P_3P_2$ | 106·0° |
| $S_1P_4S_3$ | 103·9° | $S_3P_3S_4$ | 110·8° |
| $S_2P_4S_3$ | 99·6° | $S_3P_3S_5$ | 108·4° |
| $P_1S_1P_4$ | 107·2° | $S_5P_3S_4$ | 115·0° |
| $P_2S_2P_4$ | 100·4° | $S_5P_3P_2$ | 125·5° |
| $P_3S_3P_4$ | 103·4° | $P_1P_2P_3$ | 83·0° |
| $S_1P_1P_2$ | 101·1° | $P_2P_3S_4$ | 89·6° |
| $S_1P_1S_4$ | 107·0° | $P_3S_4P_1$ | 88·7° |
| $S_2P_2P_1$ | 104·9° | $S_4P_1P_2$ | 87·0° |
| $S_2P_2P_3$ | 100·7° | | |

The crystal is monoclinic, space group $P2_1$, with a two-molecule cell, $a = 6{\cdot}412 \pm 0{\cdot}003$, $b = 10{\cdot}903 \pm 0{\cdot}005$, $c = 6{\cdot}694 \pm 0{\cdot}003$ A., $\beta = 111{\cdot}66 \pm 0{\cdot}1°$. The $^{31}$P NMR spectrum of solid $P_4S_5$ showed[971] three lines at $-200$, $-20$ and $+120$ p.p.m. with the line at $-200$ p.p.m. of greater intensity. The apical phosphorus atom was tentatively assigned to $-200$ p.p.m. and the quadruply connected atom to $+120$ p.p.m.

In all three compounds the bond lengths have been interpreted[318] as indicating no $\pi$ bonding for the cage bonds, and approximately 0·4 $\pi$ bonds/$\sigma$ bond for the apical P=S bonds.

Phosphorus sesquisulphide has been investigated by electron diffraction,[326] *X*-ray diffraction,[327–9] nuclear magnetic resonance[330, 1164] and Raman spectroscopy.[743] The molecule has a trigonal cage structure of $C_{3v}$ symmetry, containing a strained three-membered ring of phosphorus atoms. The crystal has a transition point at 39 ± 1°C.[329] and only the low-temperature modification has been investigated. This is orthorhombic, with an eight-molecule cell having $a = 9{\cdot}660$, $b = 10{\cdot}597$ and $c = 13{\cdot}671$ A. The bond lengths[329] are P–P = 2·235 A., both types of P–S = 2·090 A., and angles, P–S–P = 103·0°, S–P–S = 99·4°, S–P–P = 103·1°. The phosphorus nuclear magnetic resonance spectrum[330] confirms the structure as determined by diffraction techniques. The resonance of the ring phosphorus atoms lies at very high fields; chemical shift = +120 p.p.m. (relative to 85% orthophosphoric acid). This is probably due to the presence of bent bonds as in phosphorus. The apical phosphorus resonance lies at $-72$ p.p.m. The NMR spectrum of the rapidly rotating solid[971] gives shifts of $+103$ and $-73$ p.p.m., confirming that the shifts are little affected by the state of aggregation. The $^{31}$P NMR spectra of phosphorus–sulphur melts of different mole ratios have been used to measure the proportion of total phosphorus present as $P_4S_3$. At S/P ratios of 1·00 and 1·25, 59% and 33% respectively of the phosphorus was in this form.[1164]

The Raman spectrum[743] was determined for the solid, liquid and solution in carbon disulphide. The spectrum of the solution differed from the others, suggesting that decomposition was taking place; this was supported by a strong increase in turbidity when the solutions were irradiated. The infra-red spectrum of the solid was also reported, showing broad bands at 430 and 473 cm.$^{-1}$. The Raman spectrum was assigned on the basis of $C_{3v}$ symmetry, bands at 442, 420, 290 and 87 cm.$^{-1}$ being assigned to $A_1$ vibrations, and bands at 486, 384, 341, 221 and 154 cm.$^{-1}$ to $E$ vibrations. This assignment should not be regarded as conclusive, because the polarization data were incomplete and some assumptions were made. Approximate force constants were calculated as follow: $F_{sp}$ (apical) = 1·63 millidynes/A., $F_{sp}$ (basal) = 1·67 millidynes/A., $F_{pp}$ = 1·07 millidynes/A.

The infra-red spectra of the phosphorus sulphides have been reported.[331, 664, 1167] Absorption occurs around 530 and 686 cm.$^{-1}$ for the decasulphide, at 672–689 cm.$^{-1}$ for the heptasulphide, and at 668–674 cm.$^{-1}$ for tetraphosphorus pentasulphide.

The question of the existence of an alleged phosphorus trisulphide, $P_2S_3$ has been considered.[331] It was suggested on the basis of *X*-ray powder photographs and chromatography that this material is a mixture of other known sulphides. However, although all the lines given by this material could be assigned to $P_4S_7$ or $P_4S_5$, several of the strongest lines of these two compounds did not appear. A later report[321] describes a powder pattern which is quite distinct from those of the other phosphorus sulphides and is obtained from a new phase of variable composition $P_4S_{5\cdot5}$–$P_4S_{6\cdot75}$. This phase was prepared from melts of composition $P_4S_5$–$P_4S_{6\cdot9}$, and from the reaction of phosphorus trichloride with hydrogen sulphide. It is stable only between 200°C. and 250°C., but it is metastable for several months at room temperature. The structure is orthorhombic, with space group *Pbcn*, cell dimensions $11{\cdot}4_{(+)}$, $11{\cdot}4_{(-)}$, 8·2 A., and with four molecules (of $P_4S_{6\cdot6}$) per unit cell. The cell dimensions decrease by about 1% as the sulphur content falls from $P_4S_{6\cdot75}$ to $P_4S_{5\cdot5}$. The crystal structure of this material (of composition $P_4S_{6\cdot5}$) has recently been determined,[1165] showing it to be a defect form of $P_4S_7$. Accurate cell data are as follows: $a = 8{\cdot}14$, $b = 11{\cdot}43$, $c = 11{\cdot}39$ A., $Z = 4$ space group *Pbcn*. The molecules of $P_4S_7$ are of the same type as those in the stable heptasulphide phase, except that they possess an exact twofold axis. There is strong crystallographic evidence for a deficiency of electron density at the apical sulphur sites, in accordance with the composition. It is not known whether the deficiencies occur singly, giving defect molecules of $P_4S_6$, or in pairs, giving defect molecules of $P_4S_5$ (of a different structure from those in stable $P_4S_5$). Bond lengths are as follows: PP 2·26, PS 1·89, $P_V$–S–($P_V$) 2·12, $P_V$–S–($P_{III}$) 2·05/2·08, $P_{III}$–S–($P_V$) 2·08/2·13. The angles are similar to those in $P_4S_7$.[1163]

The radial distribution function in amorphous solid solutions of sulphur/phosphorus pentasulphide has been investigated by *X*-ray methods.[1171] It was suggested that up to 3% of phosphorus, cross-linking between the sulphur chains by short (1·9 A.) P–S bonds took place. Between 4 and 20% of phosphorus a different structure was proposed, with bonds of 2·05–2·15 A. Above 20% a 1·9 A. bond reappears, and this was taken to indicate the formation of $P_4S_{10}$ molecules.

### Phosphorus Sulphoxide

Phosphorus sulphoxide, $P_4O_6S_4$, has been examined by electron diffraction.[332] The structure is similar to that of phosphorus pentoxide with the apical oxygen atoms replaced by sulphur atoms. Bond lengths are $P{-}O = 1{\cdot}62 \pm 0{\cdot}02$ A., $P{-}S = 1{\cdot}85 \pm 0{\cdot}02$ A., and angles, $P{-}O{-}P = 123{\cdot}5 \pm 1°$, $O{-}P{-}O = 101{\cdot}5 \pm 1°$, $O{-}P{-}S = 116{\cdot}5 \pm 1°$. The angles and the P–O bond length are the same as in phosphorus pentoxide. The bond lengths lead to estimates[318] of 0·2 $\pi$ bonds/$\sigma$ bond for P–O bonds and about 1·0 $\pi/\sigma$ for P–S bonds. The crystal structure has recently been determined.[1166] The unit cell is tetragonal, with $a = 9{\cdot}065$, $c = 13{\cdot}55$ A., $Z = 4$, space group $I\bar{4}c2$. The molecules do not deviate significantly from *Td* symmetry. The molecular dimensions, in agreement with the electron diffraction results, are: $PO_{(av.)} = 1{\cdot}61$, $PS_{(av.)} = 1{\cdot}86$ A., $POP = 124{\cdot}5°$, $OPO = 100{\cdot}8°$, $OPS = 117{\cdot}2°$. An unusual feature of the structure is the fact that each molecule has near-neighbour contacts with 18 other molecules. The Raman spectrum of phosphorus sulphoxide has been reported[333] for the liquid and solid. Strongly polarized lines are found, indicating a cubic point group, consistent with the electron diffraction results. Lines at 400, 694 and 897 cm.$^{-1}$, all strongly polarized, are assigned to the three totally symmetrical ($A_1$) vibrations. Other strong lines appear at 89, 148, 353, 666 and 930 cm.$^{-1}$ The spectrum of the solid is similar to that of the liquid, and the solid is evidently also composed of discrete molecules of cubic symmetry. The stretching force constant of the P=S bond has been estimated as 5·5 millidynes/A.[320] The nuclear magnetic resonance spectrum of phosphorus sulphoxide has been investigated, and the phosphorus chemical shift reported as $-16 \pm 1$ p.p.m. (relative to 85% orthophosphoric acid).[171]

### Phosphorus Thioiodide

The crystal structure of phosphorus thioiodide, $P_4S_3I_2$, has been determined.[535] The crystal is triclinic, with a four-molecule cell having $a = 7{\cdot}31$, $b = 7{\cdot}35$, $c = 19{\cdot}61$ A., $\alpha = 94°\ 24'$, $\beta = 90°\ 10'$, $\gamma = 90°\ 55'$ and space group $P\bar{1}$. The cell contains two pairs of optical isomers, each pair related by a centre of symmetry. The molecule (Fig. 10) is composed of two five-membered rings fused to form a six-membered ring.

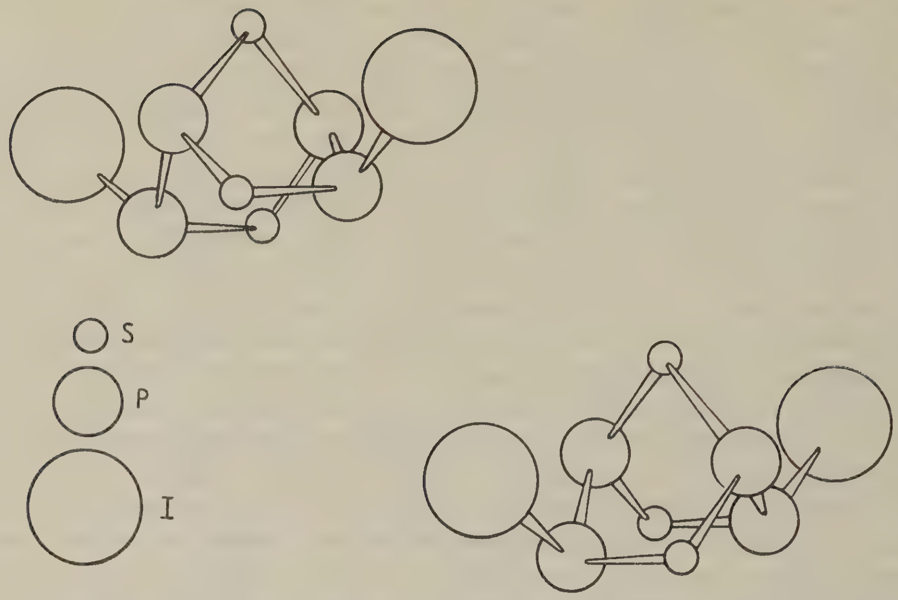
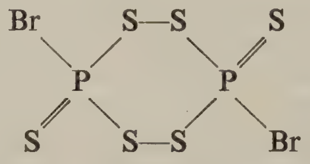


FIG. 10.—The two optically active molecules of phosphorus thioiodide, $P_4S_3I_2$

This compound may be prepared from phosphorus sesquisulphide by reaction with iodine in carbon disulphide solution, but this involves breaking a P–P bond and rearranging the skeleton, since the positions of the phosphorus and sulphur atoms in one of the five membered rings are reversed. The P–P and P–S bonds evidently have a high mobility. Bond lengths are P–I $2{\cdot}48 \pm 0{\cdot}03$, P–P $2{\cdot}20 \pm 0{\cdot}04$, P–S $2{\cdot}10 \pm 0{\cdot}04$ A.: angles S–P–S = 105°, P–S–P = 104°, P–P(I)–S = 102°, P–P(S)–S = 91°. The low value of the last angle leads to a non-bonded P–S distance of 3·1 A., 0·6 A. less than the sum of the (Pauling) Van der Waals radii.

The crystal structure of diphosphorus hexathiobromide,[1167] $P_2S_6Br_2$, has been determined.[1168] The cell is tetragonal with $a = 9{\cdot}79$, $c = 11{\cdot}51$ A., $Z = 4$, space group $P\bar{4}2_1c$. The molecules (below), which contain two PSSP bridges,



have a skew boat configuration, with average bond lengths P–Br $2{\cdot}07 \pm 0{\cdot}02$, P=S $1{\cdot}88 \pm 0{\cdot}03$, P–S $2{\cdot}10_2 \pm 0{\cdot}014$, S–S $2{\cdot}034 \pm 0{\cdot}015$ A., and angles $PSS_{(av.)}$ 99·7°, SPS 106·3°. The terminal sulphur and bromine atoms are completely disordered. The infra-red spectra of this compound, and of $P_2S_5Br_4$, have been reported.[1167]

## Phosphorus Selenide

Phosphorus sesquiselenide, $P_4Se_3$,[536] has the same space group, *Pnmb*, as the low temperature form of phosphorus sesquisulphide, but they are not isostructural. The orthorhombic sixteen-molecule cell has $a = 9{\cdot}739$, $b = 11{\cdot}797$, $c = 26{\cdot}270$ A. The molecular structure is similar to that of phosphorus sesquisulphide, and the molecules are arranged approximately in hexagonal close packing. Bond lengths are P–P = $2{\cdot}25 \pm 0{\cdot}03$ A., P–Se = $2{\cdot}24 \pm 0{\cdot}01$ A., which is in good agreement with the sum of the atomic radii. The angles are Se–P–Se = 99·9°, P–Se–P = 100·1°, Se–P–P = 105·3°, P–P–P = 60°. Infra-red and Raman data were reported[1169] for this molecule as follows: 601 (R), 525 (vw IR), 420 (w IR), 360/363 (s, R, IR), 317 (s, R, IR), 214 (? R) cm.$^{-1}$ The bands at 360 and 317 were assigned to $\nu_s(PSe_3)$ and $\nu_s(P_3Se_3)$ respectively. The $^{31}P$ NMR spectrum[1169] shows a doublet ($J = 85$ c/s) at +106 p.p.m., and quartet at −38 p.p.m., relative to 85% orthophosphoric acid, confirming the structure of the molecule. The ultra-violet spectrum[1169] shows bands at 384 (w) and 236 (s) mμ.

## ORTHOPHOSPHORIC ACID AND ORTHOPHOSPHATES

### Orthophosphoric Acid

In the monoclinic structure of anhydrous phosphoric acid,[379, 473–4] hydrogen atoms are associated with three of the oxygens of the $PO_4$ group; the P–O bond length for these oxygen atoms is 1·57 A. The other P–O bond is shorter at 1·52 A. The bond angles are 106° between the (H)–O–P bonds and 112° between these and the fourth bond. The bond lengths indicate substantial double-bond character, the shortest length evidently being an almost pure double bond.[473] The molecules are connected into sheets by hydrogen bonds of length 2·53, 2·53 (both to the 'keto' oxygen) and 2·84 A. between the 'hydroxyl' oxygens of molecules related by translation within the sheets. Structural data are summarized in Table IX.

Aqueous solutions of phosphoric acid have also been investigated[512] by *X*-rays. In 86% solution the phosphate ions are interconnected by hydrogen bonds, the O–H–O distance being 2·85 A. if the P–O distance is taken as 1·56 A. In 54% solution the ions are tetrahedrally hydrogen bonded to water molecules. The packing of unbonded oxygen atoms in neighbouring ions leads to an O–O distance of 3·2 A.

### Orthophosphates

This class of compounds includes the large group of apatites and almost all other phosphate minerals, as well as the heteropoly acids and their salts. Crystallographic data on these groups are summarized in Tables IX–XII respectively.

Two limiting kinds of crystalline orthophosphates may be distinguished: those containing isolated $PO_4^{3-}$ ions, and those in which the $PO_4$ groups share electrons with the metal atom to form a three-dimensionally bonded network similar to that of silica. The first group is typified by the orthophosphates of the alkali and alkaline-earth metals. The alkali dihydrogen orthophosphates have received considerable attention because of their ferro-electric properties; crystallographic,[390–5, 475–8, 1180] infra-red,[511, 527, 891–6, 1174–6] Raman,[1178, 1312] double-refraction dispersion,[1177] nuclear quadrupole resonance,[1179] and nuclear magnetic resonance[849–51, 883–7, 891] techniques have been employed. Slater[479] has explained the ferro-electric behaviour of potassium dihydrogen phosphate below 123°K. by assuming a double potential minimum for the O–H···O proton. The low-temperature ferro-electric phase has the protons ordered, and the high-temperature phase has them disordered, between the two potential minima. This theory has been confirmed by neutron diffraction experiments.[394, 477–8] The high polarization, however, apparently arises from displacements of other atoms, particularly the potassium atom.[510] The infra-red absorption of the OH stretching and bending vibrations does not change significantly through the Curie point.[511] The corresponding ammonium salt is apparently antiferro-electric.[403–6]

Anhydrous dicalcium phosphate, $CaHPO_4$ (monetite), has a structure[365, 852] consisting of discrete $PO_4^{3-}$ tetrahedra and $Ca^{++}$ ions, the latter co-ordinated by a shell of oxygen atoms. Double chains of Ca–$PO_4$–Ca extend along the *a* axis. The two types of calcium have respectively seven and eight nearest oxygen neighbours in their co-ordination shell. The hydrogen atoms probably lie between oxygen atoms of neighbouring phosphate groups. The structure is thus a three-dimensional network of tetrahedral $PO_4^{3-}$ anions, with $Ca^{++}$ ions in the interstices, holding the anions together by highly ionic bonds with the oxygen atoms. Nuclear magnetic resonance data have been said to indicate a change in structure with temperature[891] but later work[852] has not confirmed this. Dicalcium phosphate dihydrate, $CaHPO_4$, $2H_2O$ brushite), has a structure[367, 368, 853] in which the single Ca–$PO_4$–Ca chains are bonded together by contact between calcium and oxygen atoms in neighbouring chains resulting in a corrugated sheet of composition $CaPO_4$. These sheets are held together by the water molecules. It has recently been suggested from nuclear magnetic resonance data[545] that the single hydrogen atom is located between the oxygen atoms of two adjacent phosphate groups. A recent refinement[853] of the structure suggested that the space group was the non-centrosymmetric *Ia*, unlike the original refinement which was based on a centrosymmetrical space group. Infra-red data[852, 891] suggest a close similarity between the phosphate groups in monetite and brushite and are consistent with the existence of two or three kinds of hydrogen bond in monetite.

Anhydrous dibarium phosphate, $BaHPO_4$,[361–2] has a structure somewhat similar to that of the corresponding calcium salt with separate phosphate tetrahedra linked into chains by barium ions. The barium co-ordination, however, is different from that of calcium; each barium atom is surrounded by ten oxygen atoms, three of which are at substantially greater distances than the other seven.

Monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2,H_2O$, also has corrugated sheets of composition $CaPO_4$.[370, 852] In this case the sheets are separated by phosphate ions as well as water molecules, lowering the symmetry from monoclinic to triclinic. The corrugated sheets in these structures are very similar to the sheets of composition $CaSO_4$ which occur in gypsum.[369]

The two forms of tricalcium phosphate have not been fully investigated.[364, 480–1] The data on the $\beta$-form of tricalcium phosphate (whitlockite) are anomalous.[364] It has been suggested[1170] that the water in whitlockite is trapped and is not an essential component of the structure which was formulated as $\beta$-$Ca_3(PO_4)_2$. The structures of the analogous barium and strontium salts, $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$, have been developed on tetrahedral phosphate groups (P–O distance of 1·56 A. assumed), in an unimolecular rhombohedral cell. There are two types of metal site with twelvefold and tenfold co-ordination.

## APATITES

The most important group of phosphate minerals, the apatites, comprises a large number of different materials which preserve very closely similar structures and cell dimensions over a wide range of composition. All the structures are hexagonal, space group $P6_3/m$, with a unimolecular cell of dimensions a $\sim$ 9 A., c $\sim$ 7 A. Structural data for phosphorus-containing apatites are summarized in Table X. The general formula for an apatite is $M_{10}X_2(RO_4)_6$ where X is F, OH, Cl or Br, and R may be As, V, S or Si as well as P. The most detailed structural work has been carried out on fluorapatite, $Ca_{10}F_2(PO_4)_6$ [429, 431] and hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$.[546, 793–4, 1181] A projection of the hydroxyapatite structure down the *a* axis, based on the refinement,[546] is shown in Fig. 11.

The fluoride or hydroxyl ions are normally placed on the $6_3$ (threefold plus twofold screw) axes, at the same height ($\frac{1}{4}$ and $\frac{3}{4}$) as, and in the centre of, the triangular groups of three calcium ions. To do this with chloride ions in chlorapatite would lead to improbably short interionic distances from the calcium ions, and the chloride ions have been placed at 0 and $\frac{1}{2}$. It is doubtful if the precise locations of these ions along this axis can be regarded as fully established. Recent neutron diffraction work[1181] has shown that in hydroxyapatite the hydroxyl oxygen is displaced by about 0·3 A. from the plane of the three calcium ions. This implies a short range ordering of the hydroxyl ions.

A group of 'carbonato-apatites', some of which form the basis of mammalian bones and teeth, has been the subject of considerable controversy, and the situation is far from clear. Some authors have claimed[788, 795–6, 854–6, 1249] that the carbonate ion may replace the fluoride or hydroxyl ion in the apatite structure, particularly when the lattice is enlarged by the replacement of calcium by strontium.[796, 854, 856] Other workers[429, 797] maintain that the carbonate ions are present in macroscopic inclusions of calcium carbonate. McConnell[428, 790–2, 798–9] has pointed out that the

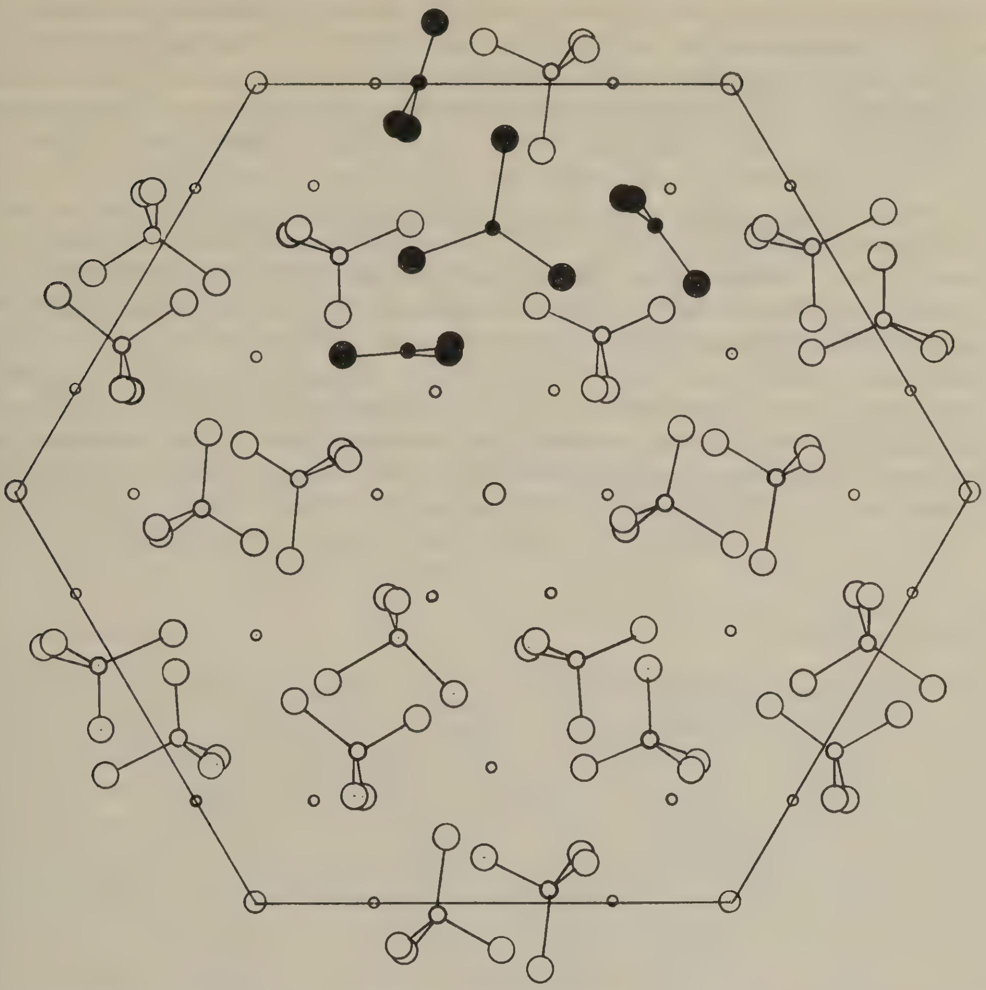


FIG. 11.—A projection of the hydroxyapatite structure[546] down the *a* axis. The upper part of the diagram shows a replacement of phosphate groups by carbonate groups, according to the ideas of McConnell[428, 790-2, 798-9] as described in the text. The carbonate oxygen atoms are shown in their original positions; slight displacement would be necessary to give the correct dimensions for the carbonate group.

⊙ oxygen in $PO_4$ groups

● oxygen in carbonate groups

○ hydroxyl

⊙ phosphorus

• carbon

∘ calcium

substitution of carbonate ions for hydroxyl ions leads to impossibly short interatomic distances, and that in some cases the total of fluoride or hydroxyl and carbonate ions exceeds the number of available sites. He has proposed a structure in which four carbon atoms replace two calcium ions and three phosphorus atoms, the carbon atoms, however, not lying on the same sites as the replaced atoms. The oxygen atoms of the displaced phosphate groups are rearranged to form carbonate groups. Such a replacement is shown in the upper part of Fig. 11. The use of formulae indicating isomorphous replacement of calcium or phosphorus by carbon is misleading since the carbon atoms do not occupy the same sites. Other workers[1182] have concluded that phosphate ions may be replaced by fluoride and hydroxyl ions as well as by carbonate groups. It has also been proposed[1183] that the phosphate groups may be replaced by the unusual ion $O_4H_4^{4-}$, for which there is evidence elsewhere.[1185–6]

The structure of apatites which are calcium-deficient has been considered by several workers.[872–6, 1184, 1246] It has been suggested, on the basis of a correlation of the intensity of an OH stretching bond in the infra-red spectrum with the Ca/P ratio,[872] that the deficiency is accounted for by hydrogen atoms which are hydrogen-bonded between the oxygen atoms of adjacent phosphate groups. This suggestion has also been made by other workers[873, 876] although there has been controversy[873–5] over the detailed interpretation of the results, and over the suggestion[873, 875–6] that there is a deficiency of hydroxyl ions as well as calcium ions. Some of the arguments used in reference 874 have recently been criticized.[877]

Octacalcium phosphate, $Ca_4H(PO_4)_3,xH_2O$, though structurally related to hydroxyapatite, is not isostructural.[1189–91] The structure is triclinic, with apatitic layers parallel to the *bc* plane, separated by hydrated layers. The hydration is not constant, and it has been suggested[1191] that part of the water is zeolitic. The unit cell dimensions of $Ca_4H(PO_4)_3,2{\cdot}5H_2O$[1189] are $a=19{\cdot}87$, $b=9{\cdot}63$, $c=6{\cdot}87_5$ A., $\alpha=89°\ 17'$, $\beta=92°\ 13'$, $\gamma=108°\ 57'$, $Z=Ca_8H_2(PO_4)_6,5H_2O$, space group $P\bar{1}$.

## SILICA-LIKE NETWORK

The three-dimensional silica-like network type of orthophosphates is typified by the phosphates of aluminium, boron, ferric iron and gallium.[350–8, 377] While the co-ordination number of the alkali and alkaline-earth metals in their phosphates lies between six and eight, in the covalent network type of phosphate the co-ordination of the metal atom is tetrahedral, like that of the phosphorus. The network is thus analogous to a $Si(SiO_4)$ network and the crystals could well be considered as double oxides. The aluminium, boron and gallium phosphates show polymorphism similar to that of silica, but ferric phosphate has so far been found only in the hexagonal low-quartz form.[351–2] Gallium phosphate has low-quartz and low-cristobalite forms stable at room temperature, and a high-cristobalite form above about 900°C.[487] The structure of the low-cristobalite form has been investigated.[377] Boron phosphate has the high cristobalite structure at room temperature,[355] but a quartz analogue has been prepared at high pressures.[356–8] Aluminium phosphate shows polymorphism almost completely analogous to that of silica, with high- and low-quartz, tridymite and cristobalite forms. The structure of the low-cristobalite form[377] is discussed below.

Bond lengths of 1·54 A. for P–O bonds and 1·44 A. for B–O bonds in high-cristobalite-type boron phosphate have been reported.[355] This P–O bond length is typical for phosphates and indicates up to $\frac{1}{3}\pi$ bond per $\sigma$ bond, which implies a shift of electronic charge into the P–O bond, making this negatively charged and the boron positive. In the low-cristobalite forms of gallium phosphate and aluminium phosphate[377] the phosphate tetrahedra were assumed to be completely regular, with a P–O distance of 1·56 A., and this led to satisfactory agreement between observed and calculated scattering intensities. The $AlO_4$ and $GaO_4$ tetrahedra were found to be somewhat distorted, but this may be exaggerated, because the distortion is probably shared between the $MO_4$ and $PO_4$ tetrahedra.

## PHOSPHORUS HETEROPOLYACIDS AND THEIR SALTS

The 12-heteropolyacids of phosphorus, of general formula $H_3(PO_4.12XO_3)_2,nH_2O$ where X = Mo or W, are composed of anions in which a central phosphate tetrahedron is surrounded by twelve interlinked octahedra of $WO_6$ or $MO_6$.[857–8] A 9(18)-heteropolyacid salt, $K_6(P_2W_{18}O_{62}),14H_2O$, has been assumed[427] to have an anion constructed from a packing of two phosphate tetrahedra surrounded by eighteen octahedra of $WO_6$ sharing edges and corners. Extensive series of hydrates are formed by these compounds; the number of water molecules per formula unit varies from 3 to 52. The crystal symmetry depends on the number of water molecules, but is frequently cubic. Hydrates with $n \leqslant 5$ are cubic with bimolecular cells. Those with $n = 29$–31 are also cubic, but with larger eight-molecule cells. Structural information on the phosphorus heteropolyacids and their salts is summarized in Table XII.

## Spectra of Orthophosphoric Acid and Phosphates

The ultra-violet absorption spectra of solutions of phosphoric acid, potassium phosphate, hydrogen phosphate and dihydrogen phosphate, and of phosphoric acid vapour have been reported[513, 515] to show absorption maxima in the region 2400–3000 Å.

The Raman spectrum[515] of anhydrous phosphoric acid changes slightly on dilution, some shifts in frequency taking place. Raman spectra have been reported for the primary, secondary and tertiary orthophosphates of the alkali metals,[515, 517–9, 521, 523, 538] for potassium deuterium phosphate,[515] and for single crystals of ammonium dihydrogen phosphate[522] as well as for the acid.[515–20, 523, 538, 609] The spectra are similar to those of phosphoric acid, with some shifts in frequency reflecting changes in symmetry and hydrogen bonding. The Raman spectra of orthophosphates show the four bands expected from tetrahedral symmetry; the $A_1$ breathing frequency gives a strong polarized line in the region 910–980 cm.$^{-1}$, the $F_2$ degenerate stretching vibration gives a weak band around 1000–1080 cm.$^{-1}$, and the $E$ and $F$ bending vibrations give bands in the 360–420 and 490–580 cm.$^{-1}$ regions respectively. In anhydrous phosphoric acid these bands are at 910, 1079, 359 and 496 cm.$^{-1}$.[516] Although no splitting of the triply degenerate stretching vibration because of changes in symmetry has been reported in the Raman spectrum, such splitting is very noticeable in the infra-red spectra of aqueous solutions of orthophosphates, in which this vibration shows up strongly.[878, 1223] Neutral salts show one band at about 1004 cm.$^{-1}$, monoacid salts two bands at about 980 and 1080 cm.$^{-1}$, with the breathing vibration weakly active at 860 cm.$^{-1}$. Diacid salts show three very strong bands at 947, 1072 and 1150 cm.$^{-1}$, as well as a 'breathing' vibration at 878 cm.$^{-1}$. Phosphoric acid itself shows the breathing vibration at 885 cm.$^{-1}$, two very strong bands at 1007 and 1165 cm.$^{-1}$, and a weak band at about 1070 cm.$^{-1}$.[878] The vibrational spectra of phosphoric acid in some non-aqueous solvents have been reported[1224] and some frequency shifts noted. The Raman spectrum of tripotassium orthophosphate shows bands at 1014, 936, 573 and 420 cm.$^{-1}$.[519] Force constants have been calculated for the phosphate ion,[523, 543–4, 879, 1224–5] but because of the variation of the frequencies with concentration and among various salts, and the use of different force fields, widely differing results have been obtained. Valence force constants calculated[1226] from the assignments[878] of aqueous solution spectra are as follows: $F_{\mathrm{PO}} = 6{\cdot}31$, $6{\cdot}97$, $7{\cdot}9$–$8{\cdot}2$, $8{\cdot}88$ millidynes/Å. for $PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^{-}$, $H_3PO_4$ respectively: $F_{\mathrm{PO(H)}} = 5{\cdot}39$, $6{\cdot}02$–$6{\cdot}14$, $7{\cdot}19$ for $HPO_4^{2-}$, $H_2PO_4^{-}$, $H_3PO_4$ respectively. The results were correlated with Cruickshank's[1227] theories of bond orders; it has recently been pointed out[1228] that a correction for the change in average force constant throughout the series is essential for this correlation.

The infra-red spectra of a large number of orthophosphates (Table XIII) have been determined, mainly for frequency correlation purposes.[524–6, 539, 745, 660] The $F_2$-type vibrations of the phosphate ion in the 1000 and 500 cm.$^{-1}$ regions are expected to be strongly active in the infra-red spectra. However, these spectra are normally obtained on the solid, and crystal coupling effects are important. Also, reduction in symmetry by hydrogen bonding may lead to a resolution of the $F_2$ bands into widely spaced components. Tribasic orthophosphates usually show a single strong band in the 1000–1060 cm.$^{-1}$ region,[524–5] with weaker absorption extending over the 1000–1150 cm.$^{-1}$ region, while acid orthophosphates show several strong peaks over the range 850–1400 cm.$^{-1}$,[525] presumably for the reasons given above. Ranges of 1010–1070 cm.$^{-1}$ and 930–990 cm.$^{-1}$ for dibasic phosphates, and 1030–90 and 900–950 cm.$^{-1}$ for monobasic phosphates, have been suggested.[524] The $F_2$-type band in the

*Table IX.—Crystallographic Data on Orthophosphates*

| Compound | Crystal system | Space group | Structure prototype | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | *a* or α | *b* or β | *c* or γ | *Z* | |
| $AcPO_4,nH_2O$ ($n<\frac{1}{2}$) | Hexagonal | | $LaPO_4^{(a)}$ | 7·22 | | 6·65 | | 347 |
| $Ag_3PO_4$ | Cubic | $P\bar{4}3n$ | | 6·00 | | | 2 | 348, 349 |
| $AgMoO_2PO_4$ | Monoclinic | $P2_1/n$ | $NaMoO_2PO_4$ | 12·142 | 11·887<br>$\beta=92{\cdot}25$ | 6·3577 | 8 | 1202 |
| $AlPO_4$ (low quartz form) (berlinite) | Trigonal | $P3_121$ | Quartz (low)$^{(b)}$ | 4·9429 | | 10·9476 | 3 | 350–354, 482–486, 841–2, 1194, 1253 |
| $AlPO_4$ (low cristobalite form) | Orthorhombic (pseudo-tetragonal) | $C222_1$ | Low cristobalite$^{(c)}$ | 7·099<br>(or 5·03 | 7·099<br>5·03 | 7·006<br>7·00 | 4<br>2) | 350, 377, 482–3, 485–6, 841–2 |
| $AlPO_4$ (high cristobalite form) | Cubic | | High cristobalite | 7·16 | | | | 482–3, 485–6, 481–2 |
| $AlPO_4,2H_2O$ (metavariscite) | Monoclinic | $P2_1/n$ | Phosphosiderite | 5·16 | 9·47<br>$\beta\sim 90°$ | 8·47 | 4 | 843 |
| $AlPO_4,2H_2O$ (variscite) | Orthorhombic | *Pcab* | Strengite, $FePO_4,2H_2O$ | 9·87 | 9·57 | 8·52 | 8 | 843 |
| $BPO_4$ | Tetragonal | *I*4 | High cristobalite$^{(d)}$ | 4·332 | | 6·640 | | 355 |
| $BPO_4$ (high press. form) | Hexagonal | | Quartz$^{(e)}$ | 4·470 | | 9·926 | 3 | 356–8 |
| $Ba_3(PO_4)_2$ | Rhombohedral | $R\bar{3}m$ | (*f*) | 7·96 (7·711)<br>42° 35′ | | | 1 | 359, 360 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $BaHPO_4$ | Orthorhombic | $Pn2_1a$ | Similarities to gypsum(g) | 14·12 | 17·15 | 4·59 | 12 | 361, 362 |
| $BiPO_4$ | Monoclinic | $P2_1/n$ | $PbCrO_4$(h) | 6·75 | 6·96<br>104° | 6·42 | | 363 |
| $\beta$-$Ca_3(PO_4)_2$ (whitlockite) | Hexagonal | $R3c$ | | 5·16 | | 18·5 | | 364, 480, 481, 1170 |
| $\alpha$-$Ca_3(PO_4)_2$ | Monoclinic | $P2_1/a$ | | 12·86 | 9·11<br>125° 30′ | 15·23 | 8 | 364 |
| $CaHPO_4$ | Triclinic | $P\bar{1}$ | (i) | 6·90<br>96° 21′ | 6·65<br>103° 54′ | 7·00<br>88° 44′ | | 365, 852 |
| $CaHPO_4,2H_2O$ (brushite) | Monoclinic | $I2/a$ or $Ia$ | Similarities to gypsum(j) | 5·812 | 15·180<br>116° 25′ | 6·239 | 4 | 366–368<br>853 |
| $Ca_3(PO_4)_2,Ca_2SiO_4$ | Hexagonal | | | 5·38 | | 7·05 | | 361 |
| $Ca(H_2PO_4)_2,H_2O$ | Triclinic | $P\bar{1}$ | (k) | 5·61<br>98° 36′ | 11·89<br>118° 0′ | 6·46<br>83° 23′ | | 370, 852 |
| $Ca(H_2PO_4)_2$, $CaCl_2,2H_2O$ | Monoclinic | $C2/c$ | | 6·41 | 17·14<br>119° 0′ | 5·76 | 2 | 452 |
| $CaBe_2(PO_4)_2$ (hurlbutite) | Orthorhombic | $Pmmm$ | | 8·29 | 8·80 | 7·81 | 4 | 397, 1195 |
| $Ca_2Fe(PO_4)_2,4H_2O$ (anapaite) | Triclinic | | | 6·39<br>101° | 6·86<br>104° | 5·89<br>71° | 1 | 1218 |
| $CaK_3H(PO_4)_2$ | Monoclinic | $C2/m$ | | 9·93 | 5·72<br>92·3° | 7·44 | 2 | 170, 1212 |
| $CaZrPO_4$ | Monoclinic | | | 9·996 | 8·774<br>$\beta$=114° 5′ | 8·323 | | 1197 |
| $CePO_4$ (I) | Monoclinic | $P2_1/n$ | | 6·76 | 7·00<br>103° 38′ | 6·44 | 4 | 371 |

Table IX.—(*continued*)

| Compound | Crystal system | Space group | Structure prototype | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | *a* or α | *b* or β | *c* or γ | *Z* | |
| $CePO_4$ (II) | Hexagonal | *C*3$_1$21 | | 7·055 | | 6·439 | 3 | 371, 372 |
| $CrPO_4$ | Orthorhombic | | | 5·15 | 7·77 | 6·11 | | 381 |
| $EuPO_4$ | Monoclinic | | monazite | 6·63 | 6·83<br>β=103° 05′ | 6·31 | 4 | 1196, 1206 |
| $FePO_4$ | Hexagonal | *C*3$_2$31 | $AlPO_4$ (low quartz form) | 5·035 | | 11·178 | 3 | 351, 352 |
| $FePO_4,2H_2O$ (phosphosiderite) | Monoclinic | *P*2$_1$/*m* | | 5·31 | 9·82<br>90° 36′ | 8·67 | 4 | 373–5, 843 |
| $FePO_4,2H_2O$ (strengite) | Orthorhombic | *Pcab* | $AlPO_4,2H_2O$ (variscite), $InPO_4,2H_2O$ | 10·07 | 9·82 | 8·67 | 8 | 375, 376, 843 |
| $Fe_3(PO_4)_2,3H_2O$ (reddingite) | Orthorhombic | *Pcmb* | | 8·73 | 10·152 | 9·57 | 4 | 382, 383 |
| $Fe_3(PO_4)_2,4H_2O$ (ludlamite) | Monoclinic | *P*2$_1$/*a* | (*l*) | 10·45 | 4·65<br>100° 30′ | 9·25 | 2 | 384–5, 1193 |
| $Fe_3(PO_4)_2,8H_2O$ (vivianite) | Monoclinic | *C*2/*m* | (*m*) | 10·08 | 13·43<br>104° 30′ | 4·70 | 2 | 386–8 |
| $GaPO_4$ (low quartz form) | Hexagonal | | $AlPO_4$ low quartz | 4·917 | | 11·10 | 3 | 487 |
| $GaPO_4$ (low cristobalite form) | Orthorhombic (pseudo-tetragonal) | *C*222$_1$ | $AlPO_4$ low cristobalite$^{(n)}$ | 6·967 | 6·967 | 6·866 | 4 | 487, 377 |
| $GaPO_4$ (high cristobalite form) | Cubic | | $AlPO_4$ high cristobalite | 7·16 at 1200°C. | | | | 487 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $GaPO_4,2H_2O$ | Monoclinic | $P2_1/n$ | (*cc*) | 9·77 | 9·64<br>β=102·7° | 9·68 | 4 | 1192 |
| $GdPO_4$ | Monoclinic | | monazite | 6·60 | 6·81<br>β=103° 28′ | 6·29 | 4 | 1196, 1206 |
| $GdPO_4$ | Hexagonal | $P6_222$ or $P6_422$ | Hexag $LaPO_4$ | 6·89 | | 6·33 | | 1256 |
| $H_3PO_4,\frac{1}{2}H_2O$ | Monoclinic | $P2_1/a$ | | 7·94 | 12·94<br>109° 25′ | 7·38 | 8 | 474 |
| $H_3PO_4$ | Monoclinic | $P2_1/c$ | (*o*) | 5·78 | 4·84<br>95° 30′ | 11·65 | 4 | 379, 473, 474 |
| $H_8(NH_4)Al_3(PO_4)_6,6H_2O$ | Hexagonal | — | | 8·90 | | 16·50 | 2 | 1286 |
| $H_8(NH_4)Fe_3(PO_4)_6,6H_2O$ | Hexagonal | — | | 9·14 | | 16·88 | 2 | 1286 |
| $H_6K_3Al_5(PO_4)_8,18H_2O$ | Hexagonal | $R3c$ or $R\bar{3}c$ | | 8·71 | | 96·1 | 6 | 1286 |
| $H_2KAl(PO_4)_2,H_2O$ | Monoclinic | $P2_1/c$ | | 10·04 | 9·10<br>β=101° 18′ | 16·34 | 8 | 1286 |
| $H_2KFe(PO_4)_2,H_2O$ | Monoclinic | $P2_1/c$ | | 10·22 | 9·23<br>β=99° 20′ | 16·56 | 8 | 1286 |
| $H_2KFe(PO_4)_2$ | Triclinic | $P1$ or $P\bar{1}$ | | 9·26<br>110° 11′ | 9·49<br>117° 7′ | 7·20<br>97° 56′ | 3 | 1286 |
| $InPO_4$ | Orthorhombic | $Cmcm$ | $CuCrO_4$^(p)^ | 5·308 | 7·851 | 6·767 | 4 | 380 |
| $InPO_4,2H_2O$ | Orthorhombic | $Pbca$ | strengite $FePO_4,2H_2O$^(q)^ | 10·36 | 8·84 | 10·19 | 8 | 859 |
| $KH_2PO_4$ (high temp. form; >123°K.) | Tetragonal | $I\bar{4}2d$ | (*r*) | 7·434<br>7·4529 ± 0·0003 | | 6·945<br>6·9751 ± 0·0006 | 4 | 390–395, 475–479, 1180 |

*Table IX.—(continued)*

| Compound | Crystal system | Space group | Structure prototype | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | *a* or $\alpha$ | *b* or $\beta$ | *c* or $\gamma$ | *Z* | |
| $KH_2PO_4$ (ferro-electric form, < 123°K.) | Orthorhombic | *Fdd* | (*s*) | 10·48 | 10·44 | 6·90 | | 390–395, 475–9 |
| $KD_2PO_4$ (high temp. form) | Tetragonal | $I\bar{4}2d$ | $KH_2PO_4$ | 7·4697 ± 0·0003 | | 6·9766 ± 0·0005 | 4 | 1180 |
| $KBaPO_4$ (low temp. form) | Orthorhombic | $P2_1cn$ or (probably) *Pmcn* | Probably $\beta$-$K_2SO_4$ | 5·615<br>$5{\cdot}66_6$ | 11·09<br>$9{\cdot}95_9$ | 7·62<br>$7{\cdot}69_7$ | 4<br>4 | 396<br>860 |
| $KBaPO_4$ (high temp. form) | Tetragonal | | | 9·84 | | 8·34 | 8 | 396 |
| $KCaPO_4$ (low) | Orthorhombic | | $K_2SO_4$ ? | 9·74 | 7·61 | 5·48 | | 396, 398 |
| $KCaPO_4$ (high) | Hexagonal | | | 5·58<br>10·60 | | 7·76<br>5·84 | <br>6 | 398<br>361 |
| $KFe_2(PO_4)_2.OH, 2H_2O$ | Monoclinic | $P2_1/n$ | | 9·76 | 9·65<br>$\beta$ = 102° 54′ | 9·70 | 4 | 1286 |
| $KSrPO_4$ (low) | Hexagonal | | | 10·70 | | 5·87 | 6 | 396 |
| $KSrPO_4$ (high) | Tetragonal | | | 9·50 | | 8·16 | 8 | 396 |
| $LaPO_4$ (I) | Monoclinic | | | 6·89 | 7·05<br>103° 34′ | 6·48 | 4 | 371 |
| $LaPO_4$ (II) | Hexagonal | $C3_121$ | | 7·081 | | 6·468 | 3 | 371 |
| $Li_3PO_4$ | Orthorhombic | | chrysoberyl $Al_2BeO_4$ $?^{(t)}$ | 4·86 | 10·26 | 6·07 | 4 | 571, 572 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $LiCoPO_4$ | Orthorhombic | *Pmnb* | $LiMnPO_4$ | | 5·87 | 10·15 | 4·68 | 4 | 1314 |
| $LiMgPO_4$ | Orthorhombic | *Pmnb* | $LiMnPO_4$ | | 5·85 | 10·03 | 4·86 | 4 | 1314 |
| $LiNiPO_4$ | Orthorhombic | *Pmnb* | $LiMnPO_4$ | | 5·92 | 10·20 | 4·70 | 4 | 1314 |
| $LiMnPO_4$ | Orthorhombic | *Pmnb* | (*u*) | 6·10 | 10·46 | 4·744 | 4 | 573, 1207 |
| $MgHPO_4,7H_2O$ (phosphorosslerite) | Monoclinic | *A*2/*a* | | 11·35 | 25·36<br>95° approx. | 6·60 | 8 | 400 |
| $Mg_3(PO_4)_2,8H_2O$ (bobierrite) | Monoclinic | | | 9·946 | 27·654<br>104° 1′ | 4·639 | | 387 |
| $MoOPO_4$ | Tetragonal | *P*4/*n* | | 6·1768 | | 4·2932 | 2 | 1204 |
| $Mo(OH)_3PO_4$ | Monoclinic | *P*2$_1$/*m* | (*v*) | 6·731 | 6·319<br>110·16° | 7·034 | | 649 |
| $(NH_4)_2HPO_4$ | Monoclinic | *P*2$_1$/*a* | | 8·03 | 6·68<br>113° 38′ | 11·02 | | 401, 402 |
| $NH_4,H_2PO_4$ (and $ND_4D_2PO_4$) room-temp. forms) | Tetragonal | *I*$\bar{4}$2*d* | (*w*) | 7·502 | | 7·546 | 4 | 403, 406 |
| $ND_4D_2PO_4$ low-temp. form (antiferro-electric) | Orthorhombic | *P*2$_1$2$_1$2$_1$ | | 7·48 | 7·48 | 7·53 | 4 | 405 |
| $(NH_4)Al_2(PO_4)_2$-$OH,2H_2O$ | Monoclinic | *P*2$_1$/*n* | | 9·63 | 9·59<br>$\beta = 103°\ 19'$ | 9·58 | 4 | 1286 |
| $Na_2HPO_4,2H_2O$ | Orthorhombic | *P*2$_1$2$_1$2 | | 10·34 | 13·64 | 16·98 | 16 | 864 |
| $NaBaPO_4$ (high) | Hexagonal<br>Tetragonal | | | 5·64<br>7·96 | | 7·35<br>8·27 | 8 | 371<br>396 |

Table IX.—(continued)

| Compound | Crystal system | Space group | Structure prototype | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | *a* or α | *b* or β | *c* or γ | *Z* | |
| $NaBePO_4$ (beryllonite) | Monoclinic | | | 8·16 | 7·79<br>90° | 14·08 | 12 | 862–3, 888–90 |
| $NaCaPO_4$ (low) | Orthorhombic | | $K_2SO_4$ ? | 9·320 | 6·830 | 5·215 | | 398, 411 |
| $NaCaPO_4$ (high) | Hexagonal | | | 10·53<br>5·23 | | 5·76<br>7·13 | 6 | 361<br>396 |
| $Na_7(PO_4)_2.F, 19H_2O$ | Cubic | *Fd*3*c* | | 27·86 | | | 40 | 636 |
| $NaMnPO_4$ (natrophyllite) | Orthorhombic | *Pbnm* | chrysoberyl $Al_2BeO_4^{(x)}$ | | | | | 408 |
| $NaMoO_2PO_4$ | Monoclinic | $P2_1/n$ | | 12·08 | 11·96<br>β=91·91° | 6·359 | 8 | 1205 |
| $NaSrPO_4$ (low) | Hexagonal | | | 10·65 | | 5·81 | 6 | 396 |
| $NaSrPO_4$ (high) | Hexagonal | | | 5·48<br>9·25 | | 7·36<br>7·93 | <br>8 | 396<br>361, 398 |
| $NaTh_2(PO_4)_3$ | Monoclinic | $C_8^4-Cc$ | | 17·39 | 6·80<br>β=101° 8′ | 8·13 | 4 | 1392 |
| $NaU_2(PO_4)_3$ | Monoclinic | $C_8^4-Cc$ | | 17·23 | 6·70<br>β=101° 22′ | 8·03 | 4 | 1392 |
| $NaWO_2PO_4$ | Monoclinic | $P2_1/n$ | $NaMoO_2PO_4$ | 12·10 | 11·96<br>β=90·75° | 6·364 | 8 | 1205 |
| $9Nb_2O_5.P_2O_5$ | Tetragonal | $I\bar{4}$ or $I4/m$ | | 15·60 | | 3·828 | | 1257 |
| $NbOPO_4$ | Tetragonal | $P4/n$ | | 6·3873 | | 4·1037 | 2 | 1211, 1217 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $NdPO_4$ (I) | Monoclinic | | monazite | 6·71 | 6·92<br>103° 28′ | 6·36 | 4 | 371, 1206 |
| $NdPO_4$ (II) | Hexagonal | | | 6·98 | | 6·34 | 3 | 371 |
| $Pb_3(PO_4)_2$ | Hexagonal | | apatite | 9·66 | | 7·11 | | 409, 410 |
| $PbHPO_4$ | Monoclinic | | | 4·65 | 6·63<br>82° 48′ | 5·76 | 2 | 361 |
| $PmPO_4$ | Monoclinic | *P*2₁/*n* | monazite | 6·72 | 6·89<br>$\beta = 104°\ 17'$ | 6·37 | 4 | 1206, 1222 |
| $PmPO_4$,0–0.5$H_2O$ | Hexagonal | *C*3₁21 | | 6·99 | | 6·35 | 3 | 1222 |
| $PrPO_4$ (I) | Monoclinic | *P*2₁/*n* | monazite | 6·75 | 6·94<br>103° 21′ | 6·40 | 4 | 371, 1206 |
| $RbH_2PO_4$ | Tetragonal | *I*$\bar{4}$2*d* | $KH_2PO_4$ | 7·58 | | 7·28 | | 414 |
| $RbBaPO_4$ | Orthorhombic | | $K_2SO_4$ | 10·60 | 7·78 | 5·73 | | 361 |
| $Sr_3(PO_4)_2$ | Rhombohedral | *R*$\bar{3}$*m* | $Ba_3(PO_4)_2$^(y)^ | 7·280<br>43° 21′ | | | 1 | 359, 360 |
| $ScPO_4$ | Tetragonal | *I*4₁/*amd* | zircon^(z)^ | 6·578 | | 5·796 | 4 | 415 |
| $SmPO_4$ | Monoclinic | | monazite | 6·66 | 6·88<br>$\beta = 103°\ 21'$ | 6·33 | 4 | 1196, 1206 |
| $TlPO_4$ | Orthorhombic | *Cmcm* | $InPO_4$^(aa)^ | 5·395 | 8·010 | 7·071 | 4 | 380 |
| $W_2O_3(PO_4)_2$ | Monoclinic | *P*2₁/*m* | (*bb*) | 7·83 | 12·48<br>91·90° | 7·76 | 4 | 650, 1203 |
| $YPO_4$ (xenotime) | Tetragonal | *I*4₁/*amd* | zircon | 6·862 | | 6·174 | 4 | 416 |
| $Zn_3(PO_4)_2,4H_2O$<br>(hopeite) | Orthorhombic | *Pnma* | | 10·62 | 18·43 | 5·02 | 4 | 417, 861,<br>1198–1200 |
| $Zr(HPO_4)_2,H_2O$ | Hexagonal | | | 10·61 | | 15·2 | 8 | 1208 |

## Footnotes to Table IX

[a] May contain up to ½ mol. of zeolitic $H_2O$.

[b] Quartz structure with alternating Al, P atoms replacing Si.

[c] Al–O–P = 145°
P–O 1·56 A.
Al–O 1·70 A.
Cristobalite structure with alternating Al, P atoms replacing Si.

[d] P–O 1·54 A.
B–O 1·44 A.
Cristobalite structure with alternating B, P atoms, replacing Si. Oxygens displaced slightly by presence of unlike atoms.

[e] Cf. $AlPO_4$.

[f] P–O 1·56 A. (assumed).
$Ba_I$–O 6 at 2·80, 6 at 3·23 A.
$Ba_{II}$–O 1 at 2·71, 3 at 2·80, 6 at 2·83 A.

[g] P–O 1·56 A.
O–O (unbonded) 3·1–3·2 A.
O–H····O 2·5 A.
Ba–O (7) 2·6–3·1 A.
(10) 2·6–3·5 A.
Separate tetrahedral $PO_4$ groups linked by H bonding to form continuous chains.
Ba co-ordination: 10 oxygens

[h] Atoms in general positions of $P2_1/n$.

[i] P–O (av.) 1·54 A.
O–O (unbonded) 2·51 A.
Independent $PO_4$ groups. Three different close O····O approaches attributed to hydrogen bonds.

[j] P–O 1·53, 1·54 A.
Corrugated sheets of composition $CaPO_4$. Water in layers between them.

[k] P–O (av.) 1·52 A.
O–O 2·48 A.
Ca–O (av.) 2·52 A.
Corrugated sheets of $CaPO_4$ (as in $CaHPO_4.2H_2O$), separated by $PO_4^{3-}$ ions and water molecules.
Tentative assignment of hydrogen atom positions.

[l] P–O 1·51–1·61 A.
Fe–O 1·99–2·30 A.
$PO_4$ tetrahedra. Octahedral co-ordination of Fe.

[m] P–O 1·57–1·68 A.
Fe–O 2·00–2·02 A.
$PO_4$ tetrahedra. Octahedral co-ordination of Fe.

[n] Ga–O–P = 135°.
Ga–O 1·78 A.
P–O 1·56 A.

[o] P–O 1·57–1·58, 1·52 A.
Trigonal symmetry of $PO_4$ ion. Hydrogen bonds between ions.

[p] P–O 1·56 A.
In–O 4 at 2·19, 2 at 1·98 A.

[q] Complex three-dimensional network, with framework of indium atoms and phosphate groups with one set of water molecules. A second set of water molecules lies in otherwise unoccupied channels of framework.

[r] P–O 1·54 A.
K and $PO_4^{3-}$ ions distributed as Zr and Si ions in zircon. Ferroelectric transition at 123°K.

[s] P–O 1·58, 1·51 A.
K and $PO_4^{3-}$ ions distributed as Zr and Si ions in zircon. Ferroelectric transition at 123°K.

[t] P–O 1·56 A.
O–P–O 110°.
$PO_4$ groups linked by tetrahedrally co-ordinated Li.

[u] P–O 1·54 A.
O–P–O 105°–113°.
Distorted $PO_4$ tetrahedral complexes. Distorted octahedral oxygen co-ordination of $Li^+$ and $Mn^{2+}$.

[v] Double chains of $MoO_6$ octahedra coupled by $PO_4$ groups. $MoO_6$ shares edges with $3PO_4$, $PO_4$ with $3MoO_6$. Chains held together by H bonding.

[w] P–O 1·53 A.
$H_2PO_4^-$ network very similar to $KH_2PO_4$. N–H···O and O–H···O bonding systems confirmed by neutron diffraction. Antiferroelectric transition at −30°C.

[x] P–O 1·59–1·66 Å.
Mn, Na–O 2·17–2·31 Å.
Mn and Na statistically distributed over 2 types of position.

[y] P–O 1·56 Å. (assumed).
$Sr_I$–O 6 at 2·63, 6 at 3·10 Å.
$Sr_{II}$–O 1 at 2·48, 3 at 2·62, 6 at 2·72 Å.

[z] P–O 1·56 Å. (assumed).
Sc–O 4 at 2·09, 4 at 2·37 Å.

[aa] P–O 1·56 Å. (assumed).
Tl–O 2 at 2·02, 4 at 2·28 Å.

[bb] $WO_6$ octahedra joined by $PO_4$ tetrahedra in 3-dimensional arrangement. $WO_6$ linked to 4 $PO_4$ and one $WO_6$, $PO_4$ to 4 $WO_6$.

[cc] Infinite double chain of $[Ga_2OH(H_2O)_2]$ connecting surrounding phosphate groups: formulation $Ga_2OH(H_2O)_2$, $(H_2O)(H)(PO_4)_2$ with $(H_2O)(H)$ disordered.

**Refs. p. 1230**

*Table X.—Structural Data on Apatites*(a)

| Compound | Unit cell data (A.) | | References |
|---|---|---|---|
| | *a* | *c* | |
| $Ca_{10}F_2(PO_4)_6$<br>Fluorapatite | 9·364 | 6·879 | 428–32 |
| $Ca_{10}Cl_2(PO_4)_6$<br>Chlorapatite | 9·52<br>10·43 | 6·85<br>7·79 | 429<br>432 |
| $Ca_{10}Br_2(PO_4)_6$<br>Bromapatite | 9·714 | 6·759 | 432 |
| $Ca_{10}(OH)_2(PO_4)_6$(b)<br>Hydroxyapatite | $9{\cdot}43_2$ | 6·88 | 428, 429, 432, 437, 546, 793, 794, 1187 |
| $Ca_{10}O(PO_4)_6$<br>Oxyapatite | 9·38 | 6·93 | 433 |
| $Ca_{10}SiP_4SO_{24}F_2$ | 9·45 | 6·96 | 1188 |
| $Ca_{10}SiP_4SO_{24}(OH)_2$ | 9·44 | 6·96 | 1188 |
| $Ba_{10}(OH)_2(PO_4)_6$ | 10·19 | 7·70 | 434 |
| $Pb_{10}Cl_2(PO_4)_6$<br>Pyromorphite | 9·95 | 7·31 | 430 |
| $Pb_{10}(OH)_2(PO_4)_6$ | 9·90 | 7·29 | 435, 437 |
| $Sr_{10}(OH)_2(PO_4)_6$ | 9·74 | 7·20 | 436 |
| $Ca_9Cd.F_2(PO_4)_6$ | 9·36 | 6·88 | 438 |
| $Ca_5Cd_5F_2(PO_4)_6$ | 9·12 | 6·71 | 438 |
| $(Sr,Ca)_{10}(OH)_2(PO_4)_6$<br>Strontium apatite<br>(11·6% SrO) | 9·41 | 6·91 | 439 |
| $(Ca,Mn)_6Ca_4F_2(PO_4)_6$<br>Mangano-apatite | 9·33 | 6·80 | 428 |
| $Ca_9(H_2O)_2(PO_4)_6$ | 9·25 | 6·88 | 433 |
| $(Sr,Ce,Na,Ca)_{10}$<br>$(OH,O)_2(PO_4)_6$<br>Belovite | 9·62 | 7·12 | 440 |
| $Ca_8Na_2P_4S_2O_{24}F_2$ | 9·52 | 6·90 | 1188 |
| $(CaSr)_6Ca_4$<br>$(F,OH,O)_2$<br>$[(P,As)O_4]_6$<br>Fermorite | 9·60 | 7·00 | 428 |
| Carbonate apatites:(c) | | | |
| Dahllite<br>'$Ca_6(OH)_2(P,C)_6O_{24}$<br>$(Ca,C)_4$' | 9·41–9·43 | 6·89–6·90 | 428, 429, 790 |
| Dehrite<br>'$(Ca,Na)_6(OH)_2(PO_4)_6$<br>$(Ca,C)_4$' | 9·31 | 6·87 | 428 |

*Table X.—(continued)*

| Compound | Unit cell data (A.) | | References |
|---|---|---|---|
| | *a* | *c* | |
| Lewistonite<br>'$(Ca,K,Na)_6(OH)_2(PO_4)_6$<br>$(Ca,C)_4$' | 9·35 | 6·89 | 428 |
| Francolite<br>'$(Ca_3F)_2(P,C)_6(O,OH,F)_{24}$<br>$(Ca,C)_4$' | 9·33–9·36 | 6·87–6·88 | 428–9, 791–2, 797, 870–1 |
| Wilkeite<br>'$Ca_6(Cl,F,OH,O)_2$<br>$(P,S,Si,C)_6O_{24}(Ca,C)_4$' | 9·48 | 6·91 | 428 |
| Ellestadite<br>'$Ca_6(Cl,F,O,OH)_2$<br>$(S,Si,P,C)_6O_{24}(Ca,C)_4$' | 9·53 | 6·91 | 428, 430 |

(a) All the apatites crystallize in the hexagonal system with space group $P6_3/m$ and one formula weight per unit cell.

(b) P–O 1·51–1·54 A.
Ca–O 2·35–2·80 A.
Ca–OH 2·35 A.

(c) A classification of carbonate apatites according to Reference 428 is as follows:

Dahllite—contains an appreciable amount of $CO_2$ and $<1\%$ F, with or without OH.
Dehrite—contains a significant replacement of Ca by Na, and with $CO_2$.
Francolite—as dahllite but $>1\%$ F.
Lewistonite—contains an appreciable amount of K, with or without $CO_2$.

*Table XI.—Structural Data on Phosphate Minerals (excluding Apatites)*

| Mineral | Crystal system | Space group | Structure prototype | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | *a* or *α* | *b* or *β* | *c* or *γ* | *Z* | |
| Abukamalite, $CaY_2(Si,P)_2O_8$ | Hexagonal | | | 5·7 | | 8·1 | | 729 |
| Amblygonite, $LiAl(PO_4)(OH,F)$ | Triclinic | $P\bar{1}$ | | 5·18<br>112° 07′ | 7·15<br>97° 48′ | 5·04<br>67° 53′ | | 459, 460 |
| Ardealite, $Ca_2H(PO_4)(SO_4),4H_2O$ | Monoclinic | | Brushite, $CaHPO_4,2H_2O$ | 5·67 | 14·64 | 6·28 | 4 | 742 |
| Autunite, $Ca(UO_2)_2(PO_4)_2,10\frac{1}{2}H_2O$ | Tetragonal | $I4/mmm$ | (*a*) | 6·989 | | 20·63 | 2 | 444 |
| Avelinoite, $NaFe_3(PO_4)_2(OH)_4,2H_2O$ | Tetragonal | $P4_1$ | Wardite | 7·32 | | 19·4 | 4 | 462, 721 |
| Barium uranite, | | | | | | | | |
| $Ba(UO_2)_2(PO_4)_2,2H_2O$ | Tetragonal | | Autunite ?$^{(b)}$ | 6·952 | | 8·515 | | 444 |
| $Ba(UO_2)_2(PO_4)_2,6H_2O$ | Tetragonal | | Autunite ?$^{(b)}$ | 6·952 | | 8·515 | | 444 |
| Barbosalite, $FeFe_2(PO_4)_2OH_2$ | Monoclinic | $P2_1/c$ | Lazulite | 7·25 | 7·46<br>120° 15′ | 7·49 | | 866 |
| Bassettite, $Fe(UO_2)_2(PO_4)_2,8H_2O$ | Monoclinic (pseudo-tetragonal) | | | 6·98 | 17·07<br>90° 32′ | 7·01 | | 728 |
| Berlinite, $AlPO_4$$^{(c)}$ | | | | | | | | |
| Bermanite, $(Mn,Mg)_5Mn_8(PO_4)_8(OH)_{10},15H_2O$ | Orthorhombic | | | 6·25 | 8·92 | 19·61 | | 468 |
| Beryllonite, $NaBePO_4$$^{(c)}$ | | | | | | | | |
| Bobierrite, $Mg_3(PO_4)_2,8H_2O$$^{(c)}$ | | | | | | | | |
| Bøggildite, $Na_2Sr_2Al_2(PO_4)F_9$ | Monoclinic (pseudo-orthorhombic) | $P2_1/c$ | (*d*) | 5·24 | 10·48<br>107·35° | 18·52 | 4 | 727 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Brazilianite, $NaAl_3(OH)_4(PO_4)_2$ | Monoclinic | $P2_1/n$ | | 11·19 | 10·08<br>97°22′ | 7·06 | 4 | 463 |
| Brushite, $CaHPO_4,2H_2O$[(c)] | | | | | | | | |
| Chalcosiderite, $CuFe_6(OH)_8(PO_4)_4,4H_2O$ | Triclinic | | | 7·66 | 10·20 | 7·89 | | 455 |
| Childrenite, $AlPO_4Fe(OH)_2,2H_2O$ | Orthorhombic (pseudo ?) | $Bba2$ or $Bbam$ | | 10·38 | 13·36 | 6·911 | 8 | 441–3, 868 |
| Chinoite, $Cu_5(OH)_4(PO_4)_2$ | Orthorhombic | $Pnn$ | | 7·47 | 8·31 | 5·83 | 2 | 453 |
| Chlor-spodiosite, $Ca_3(PO_4)_2CaCl_2$ | Orthorhombic | $Pbcm$ | | 6·17 | 6·89 | 10·74 | 4 | 451, 452 |
| Churchite, $(Y, Er)PO_4,2H_2O$ (Weinshenkite) | Monoclinic | | Brushite, $CaHPO_4,2H_2O$ | 5·46 | 15·12<br>113° 24′ | 6·28 | 4 | 735, 736 |
| Cornetite, $Cu_3PO_4(OH)_3$ | Orthorhombic | $Pbca$ | | 10·845 | 14·045 | 7·081 | 8 | 1220, 1221 |
| Deltaite, $Ca_2Al_2(PO_4)_2(OH)_4,H_2O$ | Hexagonal | $R\bar{3}m$ | | 6·98 | | 16·1 | | 738 |
| Eosphorite, $AlPO_4(Mn, Fe)(OH)_2,H_2O$ | Orthorhombic (pseudo ?) | $Bbam$ | Childrenite[(e)] | 10·52 | 13·60 | 6·97 | 8 | 867 |
| Faheyite, $(Mn, Mg, Na)Be_2F_2(PO_4)_4,6H_2O$ | Hexagonal | | | 9·43 | | 16·00 | | 470 |
| Frondelite, $Mn^{II}, Fe^{III}{}_4(OH)_5(PO_4)_3$ | Orthorhombic | $B22_12$ | | 13·89 | 17·01 | 5·21 | | 469 |
| Graftonite, $(Fe, Mn, Ca)_3(PO_4)_2$ | Monoclinic | | | 8·89 | 11·57<br>99° 6′ | 6·16 | | 722 |
| Griphite, $(Na, Ca, Fe, Al)_6Mn_4(PO_4)_5(OH, F)_8$ | Cubic | $Ia3d$ | | 12·3 | | | | 741 |
| Goyazite, $SrAl_3(PO_4)_2(OH)_5,H_2O$ | Hexagonal | $R\bar{3}m$ | | 6·97 | | 16·5 | | 737 |
| Herderite, $CaBePO_4(F, OH)$ | Monoclinic | $P2_1/c$ | Datolite, $CaOH_{13}SiO_4$ | 4·80 | 7·68<br>90° 6′ | 9·80 | 4 | 154, 1254 |

Table XI.—(continued)

| Mineral | Crystal system | Space group | Structure prototype | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | a or α | b or β | c or γ | Z | |
| Hopeite, $Zn_3(PO_4)_2,4H_2O^{(c)}$ | | | | | | | | |
| Hureaulite, $(Mn, Fe)_5H_2(PO_4)_4,4H_2O$ | Monoclinic | *P2/n* | | 17·40 | 9·06<br>96° 85′ | 9·49 | | 723 |
| Hurlbutite, $CaBe_2(PO_4)_2^{(c)}$ | | | | | | | | |
| Iron lazulite, $(Fe, Mg)O.Al_2O_3.P_2O_5,H_2O$ | Tetragonal | *I4₁22* | | 5·37 | 12·81 | | | 456 |
| Iron sicklerite, $(Li, Mn)FePO_4$ | Orthorhombic | *Pbnm* | Chrysoberyl, $Al_2BeO_4$ | 4·787 | 10·086 | 5·939 | | 412 |
| Isokite, $CaMgPO_4F$ | Monoclinic | *C2/c* | | 6·52 | 8·75<br>$\beta = 121°\ 28'$ | 7·51 | | 1255 |
| Laueite, $FeMn_2(OH)_2(PO_4)_2,8H_2O$ | Triclinic | | | 5·28<br>107° 55′ | 10·66<br>110° 59′ | 7·14<br>71° 7′ | | 457, 1213–5 |
| Lazulite, $MgAl_2(PO_4)_2(OH)_2$ | Monoclinic | *P2₁/c* | (*f*) | 7·16 | 7·26<br>120° 40′ | 7·24 | | 740, 866 |
| Libethenite, $Cu_2(OH)PO_4$ | Orthorhombic | *Pnnm* | | 8·43 | 8·08 | 5·90 | | 154, 1219 |
| Liroconite, $Cu_2Al(As, P)O_4(OH)_4,4H_2O$ | Monoclinic | *I2/a* | | 12·70 | 7·57<br>91° 23′ | 9·88 | 4 | 454 |
| Ludlamite, $Fe_3(PO_4)_2,4H_2O^{(c)}$ | | | | | | | | |
| Metauranocircite, | | | | | | | | |
| $Ba(UO_2)_2(PO_4)_2,8H_2O$ | Tetragonal | *P4nmm* | | 6·96 | | 16·90 | 2 | 446 |
| $Ba(UO_2)_2(PO_4)_2,10H_2O$ | Tetragonal | *P4₂2* | | 6·96 | | 17·57 | 2 | 446 |
| Meta-autunite I, $Ca(UO_2)_2(PO_4)_2,6\frac{1}{2}H_2O$ | Tetragonal | *P4/nmm* | (*a*) | 6·980 | | 8·420 | 1 | 444 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Meta-autunite II, $Ca(UO_2)_2(PO_4)_2,2\frac{1}{2}H_2O$ | Orthorhombic | | (*a*) | 6·45 | 6·97 | 8·65 | | 154 |
| Monazite, (La, Ce, Y)$PO_4$ | Monoclinic | | | 6·782 | 6·993<br>103° 38′ | 6·455 | | 371, 399, 407 |
| Moraesite, $Be_2PO_4(OH),4H_2O$ | Monoclinic | | | 8·55 | 36·90<br>97° 41′ | 7·13 | 12 | 447 |
| Natrophyllite, $NaMnPO_4$(c) | | | | | | | | |
| Ningyoite, $U_{1-x}Ca_{1-x}(R.E)_{2x}(PO_4)_2,1\text{–}2H_2O$ ($x=0{\cdot}1\text{–}0{\cdot}2$) | Orthorhombic (pseudo-hexagonal) | probably *P*222 | | 6·78 | 12·10 | 6·38 | 3 | 726 |
| Overite, $Ca_3Al_6(PO_4)_8,20H_2O$ | Orthorhombic | | | 14·62 | 18·68 | 7·08 | 2 | 448 |
| Phosphophyllite, $Zn_2Fe(PO_4)_2,4H_2O$ | Monoclinic | *P*2₁/*c* | | 10·23 | 5·08<br>120° 15′ | 10·49 | 4 | 389, 869, 1201 |
| Phosphorosslerite, $MgHPO_4,7H_2O$(c) | | | | | | | | |
| Phosphosiderite, $FePO_4,2H_2O$(c) | | | | | | | | |
| Phosphuranylite, $Ca(UO_2)_4OH_4(PO_4)_2$ | Orthorhombic | *Bmmb* | | 15·85 | 17·42 | 13·76 | | 725 |
| Pseudolaueite, $MnFe_2(OH)_2(PO_4)_2,8H_2O$ | Monoclinic | | | 9·57 | 7·45<br>104° 40′ | 10·16 | | 724 |
| Reddingite, $Fe_3(PO_4)_2,3H_2O$(c) | | | | | | | | |
| Sabugalite, $H\,Al(UO_2)_4(PO_4)_4,16H_2O$ | Tetragonal | | (*g*) | 6·69 | | 19·3 | 1 | 458 |
| Saleite, $Mg(UO_2)_2(PO_4)_2,10\frac{1}{2}H_2O$ | Tetragonal | | (*g*) | 6·980 | | 19·813 | 2 | 464, 458 |
| Scholzite, $Ca_6Zn_2(OH)_4(PO_4)_4,2H_2O$ | Monoclinic (pseudo-orthorhombic) | | | 6·46 | 9·05 | 7·55 | | 733 |
| $CaZn_2(PO_4)_2,2H_2O$ | Orthorhombic | *Pbmm* or *Pbnm* | | 17·14 | 22·19 | 6·61 | 12 | 734 |

*Table XI.—(continued)*

| Mineral | Crystal system | Space group | Structure prototype | Unit cell data (dimensions in Å.) | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | *a* or α | *b* or β | *c* or γ | *Z* | |
| Scorzalite, $FeAl_2(PO_4)_2(OH)_2$ | Monoclinic | $P2_1/c$ | Lazulite | 7·15 | 7·31<br>β=120° 35′ | 7·25 | | 740, 866 |
| Silicocarnotite, $Ca_3(PO_4)_2Ca_2SiO_4$ | Orthorhombic | *Pnnn* | | 10·1 | 6·7 | 15·4 | 4 | 450 |
| Sodium uranospinite, $(Na_2Ca)O(UO_2)_2[(As, P)O_4]_2,5{\cdot}2H_2O$ | Tetragonal | | | | | | | 732 |
| Strengite, $FePO_4,2H_2O^{(c)}$ | | | | | | | | |
| Strunzite, $(Mn^{2+}Fe^{2+})Fe_2{}^{3+}(PO_4)_2(OH, O)_2,8H_2O$ | Monoclinic | probably C2/*c* | | 9·80 | 18·06<br>100° 10′ | 7·34 | 8 | 730 |
| Svanbergite, $SrAl_3(OH)_6(SO_4)(PO_4)$ | Trigonal | *R*3*m* | | 6·96 | | 16·8 | 3 | 449, 471 |
| Tarbuttite, $Zn_2(OH).PO_4$ | Triclinic | | | 8·097<br>89° 34½′ | 12·91<br>91° 37½′ | 7·688<br>107° 47′ | 8 | 472 |
| Triphylite, $Li(Mn, Fe)PO_4$ | Orthorhombic | *Pbnm* | Chrysoberyl, $Al_2BeO_4^{(h)}$ | 4·711<br>4·72 | 10·374<br>10·36 | 6·038<br>6·02 | | 412, 413, 722 |
| Triploidite, $(Mn, Fe)_2(OH)PO_4$ | Monoclinic | 1*b* | Titanite, $CaTiOSiO_4$ | 12·10 | 13·13<br>108° 18′ | 9·71 | | 466, 467 |
| Turquoise, $CuAl_6(OH)_8(PO_4)_4,5H_2O$ | Triclinic | | | 7·48<br>111° 39′ | 9·95<br>115° 23′ | 7·68<br>69° 26′ | | 455 |
| Uranocircite, $Ba(UO_2)_2(PO_4)_2,8H_2O$ | Tetragonal | *P*4/*mmm* | | 6·95 | | 8·44 | 1 | 445 |
| Variscite, $AlPO_4,2H_2O^{(c)}$ | | | | | | | | |
| Vavryenite, $(Mn, Fe)BePO_4.OH$ | Monoclinic | $P2_1/a$ | (*i*) | 5·411 | 14·49<br>102° 45′ | 4·730 | 4 | 865, 888 |
| Viséite, $Na_2Ca_{10}[Al_{20}Si_6P_{10}H_{36}]O_{46}$ | Cubic or pseudo-cubic | | | 13·65 | | | | 731 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Vivianite, $Fe_3(PO_4)_2,8H_2O$[c] | | | | | | | | |
| Wagnerite, $Mg(MgF)PO_4$ | Monoclinic | *C*2/*c* | Titanite, $CaTiOSiO_4$ | 11·90 | 12·51<br>108° 7′ | 9·63 | 4 | 465 |
| Wardite, $NaAl(PO_4)_2(OH)_4,2H_2O$ | Tetragonal | *P*4 | | 7·04 | | 18·88 | 4 | 461 |
| Whitlockite, $\beta$-$Ca_3(PO_4)_2$[c] | | | | | | | | |
| Woodhouseite, $CaAl_3(PO_4)(SO_4)(OH)_6$ | Trigonal | *R*3*m* | | 6·96 | | 16·8 | 3 | 449 |
| Xenotime, $YPO_4$[c] | | | | | | | | 1216 |

[a] Built up of $UO_2PO_4$ sheets spread normal to *c* axis, held together by Ca atoms between sheets (cf. mica and other platy silicates).

[b] Analogous and partly isomorphous with corresponding Ca compounds (autunites).

[c] See Table IX.

[d] Weak extra lines may be due to twinning or superstructure.

[e] Two parallel sets of infinite chains, one of $MnFeO_4(OH)_2$ octahedra sharing opposite O–O edges, the other of $AlO_2(OH)_2(H_2O)_2$ octahedra sharing opposite $H_2O$ corners; chains alternate sharing OH corners to form parallel sheets held together by $PO_4$ groups.

[f] Metal–oxygen octahedra and $PO_4$ tetrahedra share corners to produce sheets and tie these into a three-dimensional network.

[g] Autunite-like.

[h] P–O 1·49–1·58 in $PO_4$, Fe–O 2·08–2·28, Li–O 2·10–2·26. Sixfold O co-ordination of Fe and Li.

[i] Chains of $BeO_2(OH)_2$ and $PO_4$ tetrahedra linked by Al–O bonds.

*Table XII.—Structural Data on Phosphorus Heteropolyacids and Salts*

| Compound | Crystal system | Space group | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|
| | | | *a* or α | *b* or β | *c* or γ | *Z* | |
| $Ba_3(PO_4.12WO_3)_2,48H_2O$ | Hexagonal | | 15·31 | | 41·16 | 3 | 418 |
| $Ba_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·10 | | | 4 | 418 |
| $Ca_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·11 | | | 4 | 418 |
| $Cd_3(PO_4.12WO_3)_2,48H_2O$ | Hexagonal | | 15·51 | | 41·04 | 3 | 418 |
| $Cd_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·13 | | | 4 | 418 |
| $Co_3(PO_4.12WO_3)_2,48H_2O$ | Hexagonal | | 15·48 | | 41·07 | 3 | 418 |
| $Co_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·11 | | | 4 | 418 |
| $Cs_3PO_4.12WO_3,nH_2O(n \leqslant 2)$ | Cubic | | 11·830 | | | 2 | 419 |
| $GdPO_4.12MoO_3,3H_2O$ | Cubic | *Fd3m* | 23·1 | | | 8 | 420 |
| $H_3PO_4.12MoO_3,3H_2O$ | Cubic | *Fd3m* | 23·281 | | | 8 | 420 |
| $H_3PO_4.12WO_3,5H_2O$ | Cubic | | 12·141 | | | 2 | 421 |
| $H_3PO_4.12MoO_3,14H_2O$ | Triclinic | | 20·12 | 19·25 | 22·55 | 8 | 422 |
| | | | 95° 17′ | 96° 37′ | 92° 53′ | | |
| $H_3PO_4.12WO_3,14H_2O$ | Triclinic | | 20·48 | 19·32 | 22·48 | 8 | 422 |
| | | | 95° 37′ | 95° 9′ | 90° 16′ | | |
| $H_3PO_4.12WO_3,21H_2O$ | Orthorhombic | | 20·84 | 13·07 | 18·95 | 4 | 423 |
| $H_3PO_4.12WO_3,24H_2O$ | Trigonal | | 15·80 | | | 2 | 424 |
| | | | 58° 36′ | | | | |
| $H_3PO_4.12WO_3,29H_2O$ | Cubic | | 23·30 | | | | 424, 425 |
| $K_3PO_4.12WO_3,4H_2O$ | Cubic | | 11·72 | | | 2 | 426 |
| $K_3PO_4.12MoO_3,4H_2O$ | Cubic | | 11·70 | | | 2 | 426 |
| $K_6(PO_4)_2.18WO_3,14H_2O$[a] | Triclinic | $P\bar{1}$ | 12·86 | 14·83 | 22·34 | | 427 |
| | | | 94° 24′ | 116° 53′ | 115° 36′ | | |
| $Mg_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·11 | | | 4 | 418 |
| $Mn_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·11 | | | 4 | 418 |
| $Mn_3(PO_4.12WO_3)_2,48H_2O$ | Hexagonal | | 15·50 | | 41·08 | 3 | 418 |
| $(NH_4)_3.PO_4.12WO_3,4H_2O$ | Cubic | | 11·83 | | | 2 | 426 |
| $NdPO_4.12WO_3,3H_2O$ | Cubic | *Fd3m* | 23·10 | | | 8 | 420 |
| $Ni_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·11 | | | 4 | 418 |
| $Ni_3(PO_4.12WO_3)_2,48H_2O$ | Hexagonal | | 15·51 | | 41·19 | 3 | 418 |
| $SmPO_4.12MoO_3,3H_2O$ | Cubic | *Fd3m* | 23·1 | | | 8 | 420 |
| $Sr_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·10 | | | 4 | 418 |
| $Tl_3PO_4.12MoO_3,4H_2O$ | Cubic | | 11·60 | | | 2 | 426 |
| $Tl_3PO_4.12WO_3,4H_2O$ | Cubic | | 11·89 | | | 2 | 426 |
| $Zn_3(PO_4.12MoO_3)_2,58H_2O$ | Cubic | | 23·10 | | | 4 | 418 |

(a) Packing of $PO_4$ tetrahedra and $WO_6$ octahedra sharing edges and corners.

*Table XIII.—Infra-red Spectra of Orthophosphates*

| Compound | Reference |
|---|---|
| $Ag_3PO_4$ | 525–6, 559, 745–6 |
| $AlPO_4$ | 746, 1247 |
| $BPO_4$ | 745–6 |
| $Ba_3(PO_4)_2$ | 525, 746 |
| $Ba_3(PO_4,AsO_4)_2$ | 1234 |
| $Ba(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $BaHPO_4$ | 530 |
| $BaDPO_4$ | 530 |
| $Be_3(PO_4)_2$ | 1243 |
| $Be(H_2PO_4)_2$ | 1243 |
| $Be(HPO_4),nH_2O$ | 1243 |
| $BeOH(H_2PO_4)$ | 1243 |
| $BiPO_4$ | 745–6 |
| $Bi(PO_4,AsO_4)$ | 1234 |
| $Ca_4H(PO_4)_3,xH_2O$ | 1233, 1236, 1246 |
| $Ca_3(PO_4)_2$ | 524–5, 745–6, 876, 880 |
| $CaDPO_4$ | 1231 |
| $CaDPO_4,2H_2O$ | 1231 |
| $Ca(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $CaHPO_4$ | 525, 747, 852, 891, 1231 |
| $CaHPO_4,2H_2O$ | 524, 531, 747, 852, 880, 1230, 1231, 1235, 1237 |
| $Ca(H_2PO_4)_2$ | 525, 747 |
| $Ca(H_2PO_4)_2,H_2O$ | 524, 525, 852, 880 |
| $Cd_3(PO_4)_2$ | 746 |
| $CePO_4$ | 746, 1240 |
| $CePO_4,2H_2O$ | 1240 |
| $Ce_3(PO_4)_2$ | 746 |
| $Co_3(PO_4)_2,8H_2O$ | 745–6 |
| $Co_2(PO_4)_2$ | 880 |
| $Co(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $CrPO_4$ | 746 |
| $CrPO_4,H_2O$ | 524 |
| $CrPO_4,3H_2O$ | 746 |
| $CrPO_4,6H_2O$ | 525, 746, 1248 |
| $Cr_2O_33P_2O_5,19H_2O$ | 1248 |
| $Cu_3(PO_4)_2$ | 745–6 |
| $Cu_3(PO_4)_2,3H_2O$ | 524, 880 |
| $D_3PO_4$ | 540 |
| $DyPO_4$ | 1240 |
| $DyPO_4,2\frac{1}{2}H_2O$ | 1240 |
| $ErPO_4$ | 1240 |
| $ErPO_4,xH_2O$ | 1240 |
| $EuPO_4$ | 1240 |
| $EuPO_4,\frac{3}{2}H_2O$ | 1240 |
| $Fe_3(PO_4)_2$ | 746 |
| $FePO_4$ | 746 |
| $FePO_4,2H_2O$ | 525, 1247 |
| $FeNH_4PO_4,H_2O$ | 525 |
| $GdPO_4$ | 1240 |
| $GdPO_4,\frac{3}{2}H_2O$ | 1240 |
| $H_8(NH_4,K)Fe_3(PO_4)_6,6H_2O$ | 1247 |
| $H_4CaFe_2(PO_4)_4,5H_2O$ | 1247 |
| $H_3PO_4$ | 514, 897, 1241 |
| $Hg_3PO_4$ | 745–6 |
| $HoPO_4$ | 1240 |
| $HoPO_4,2H_2O$ | 1240 |
| $K_3Al_5H_6(PO_4)_8,18H_2O$ | 1242 |
| $K_3PO_4$ | 524, 880 |
| $K_2DPO_4$ | 530 |
| $K_2HPO_4$ | 526, 530, 747, 880, 1229 |
| $K_2HPO_4,3H_2O$ | 530, 747 |
| 'basic potassium aluminium phosphate' | 1247 |
| $KAl_2(PO_4)_2OH,2H_2O$ | 1247 |
| $KH_2PO_4$ | 511, 524–5, 527–9, 747, 891–6, 1175–6, 1178 |
| $LaPO_4$ | 745–6, 1240 |
| $LaPO_4,\frac{3}{2}H_2O$ | 1240 |
| $Li_3PO_4$ | 525, 745–6 |
| $LuPO_4$ | 1240 |
| $LuPO_4,xH_2O$ | 1240 |
| $Mg_3(PO_4)_2$ | 525, 745–6 |
| $Mg_3(PO_4)_2,4H_2O$ | 524 |
| $Mg(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $MgHPO_4,3H_2O$ | 524 |
| $MgNH_4PO_4,6H_2O$ | 525 |
| $Mg(H_2PO_4)_2$ | 524 |
| $Mn_3(PO_4)_2$ | 746 |
| $Mn_3(PO_4)_2,7H_2O$ | 524, 745 |
| $Mn(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $Na_3PO_4$ | 525, 745, 880 |
| $Na_3PO_4,12H_2O$ | 524, 746, 880, 897 |
| $Na_2HPO_4$ | 525, 747 |
| $Na_2HPO_4,2H_2O$ | 525 |
| $Na_2HPO_4,12H_2O$ | 524, 747, 897 |
| $NaH_2PO_4$ | 525, 747, 880, 891–2 |
| $NaH_2PO_4,H_2O$ | 524, 747 |
| $NaH_2PO_4,2H_2O$ | 525, 897 |
| $Na(NH_4)HPO_4,4H_2O$ | 747 |
| $Na_2NH_4PO_4$ | 880 |
| $NdPO_4$ | 745–6, 1240 |
| $NdPO_4,\frac{3}{2}H_2O$ | 1240 |
| $(NH_4)_3PO_4$ | 746 |
| $(NH_4)_3Al_5H_6(PO_4)_8,18H_2O$ | 1242 |
| $(NH_4)_2HPO_4$ | 524–5, 747, 880, 897, 1229 |
| $(NH_4)_2AlH(PO_4)_2,4H_2O$ | 1242 |
| $NH_4BePO_4,nH_2O$ | 1243 |
| $NH_4AlPO_4OH,2H_2O$ | 1242 |
| $NH_4AlPO_4OH,3H_2O$ | 1242 |
| $NH_4H_2PO_4$ | 524–5, 528–9, 891–2, 895, 1178 |
| $Ni_3(PO_4)_2$ | 1245 |

*Table XIII.—(continued)*

| Compound | Reference |
|---|---|
| $Ni_3(PO_4)_2,7H_2O$ | 524 |
| $Ni_3(PO_4)_2,8H_2O$ | 745–6 |
| $NiHPO_4$ | 1245 |
| $Ni(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $NiNH_4PO_4$ | 1245 |
| $NiNaPO_4$ | 1245 |
| $Pb_3(PO_4)_2$ | 524–5 |
| $PrPO_4$ | 1240 |
| $PrPO_4,2H_2O$ | 1240 |
| $SmPO_4$ | 1240 |
| $SmPO_4,\frac{3}{2}H_2O$ | 1240 |
| $SnHPO_4$ | 747 |
| $Sr_3(PO_4)_2$ | 525, 745 |
| $Sr_3(PO_4,AsO_4)_2$ | 1234 |
| $Sr(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $TbPO_4$ | 1240 |
| $TbPO_4,\frac{3}{2}H_2O$ | 1240 |
| $Th_3(PO_4)_4,4H_2O$ | 746 |
| $Tl_3PO_4$ | 526, 745–6 |
| $TmPO_4$ | 1240 |
| $TmPO_4,2H_2O$ | 1240 |
| $U,2UO_2H_3(PO_4)_3$ | 747 |
| $YPO_4$ | 1240 |
| $YPO_4,3H_2O$ | 1240 |
| $YbPO_4$ | 1240 |
| $YbPO_4,xH_2O$ | 1240 |
| $Zn_3(PO_4)_2$ | 526 |
| $Zn(GePO_4(HPO_4))_2,xH_2O$ | 1244 |
| $Zn(H_2PO_4)_2$ | 747 |
| Phosphomolybdic acid $H_3PMo_{12}O_{40},29H_2O$ | 880, 1258 |
| $Ca_{10}F_2(PO_4)_6$ (fluorapatite) | 789, 880, 882, 1232 |
| $Ca_{10}(OH)_2)(PO_4)_6$ (hydroxyapatite) | 788–9, 872–6, 880–2, 1232, 1236, 1238–9, 1246, 1249 |
| Synthetic 'carbonate apatite' | 788 |
| Barrandite | 1247 |
| Leucophosphites (K, $NH_4$) | 1247 |
| Metavariscite | 1247 |
| Phosphosiderite | 1247 |
| Phosphotridymite | 1247 |
| Strengite | 1247 |
| Taranakites (K, $NH_4$) | 1247 |
| Variscite | 1247 |
| Wavellite | 1247 |

500 cm.$^{-1}$ region gives absorption, often with several unresolved bands, in the region 520–620 cm.$^{-1}$ in many phosphates.[660, 745]

The spectra of a number of crystalline phosphates have been studied in considerable detail. Partial assignments have been reported[1229] for dipotassium and diammonium hydrogen phosphates, assuming the potassium salt to have the same space group ($P2_1/a$) as the ammonium salt. Dicalcium phosphate $CaHPO_4$ (monetite)[1231] and its dihydrate (brushite)[1230–1] have been investigated and complete assignments proposed. The factor group splitting in brushite was interpreted[1230] as evidence that the space group was $Ia$ rather than $I2/a$. In synthetic hydroxyapatite and mineral fluorapatite, an infra-red study[1232] and site symmetry analysis suggested that the symmetry of the phosphate ion was lowered to $C_s$ in fluorapatite and $C_1$ in hydroxyapatite, in accordance with the neutron diffraction data.[1181] The infra-red spectrum of octacalcium phosphate indicates[1233] that the symmetry is lowered to $C_1$ for all the phosphate species in the unit cell, in accordance with the crystal structure.[1189] The factor group splitting which causes broad bands in many crystalline phosphates has been eliminated in a number of cases[1234] by diluting the phosphate groups with arsenate groups in a mixed crystal, enabling the site symmetry to be observed directly. In the infra-red spectra of a number of anhydrous phosphates[1287] the selection rules were observed to follow the site symmetry.

Aqueous orthophosphoric acid was at one time used in nuclear magnetic resonance measurements as a standard for $^{31}P$ chemical shift determinations. The shift of 85% orthophosphoric acid was taken as zero, and other orthophosphates then lie between $\pm 5$ p.p.m.[171] The effect of the degree of ionization of phosphates on the chemical shift has been investigated,[532, 739, 1250] enabling orthophosphoric acid to be used as an internal standard in aqueous solutions. The chemical shift changes smoothly from 0 to $-6$ p.p.m. as alkali is added. If the chemical shift is plotted

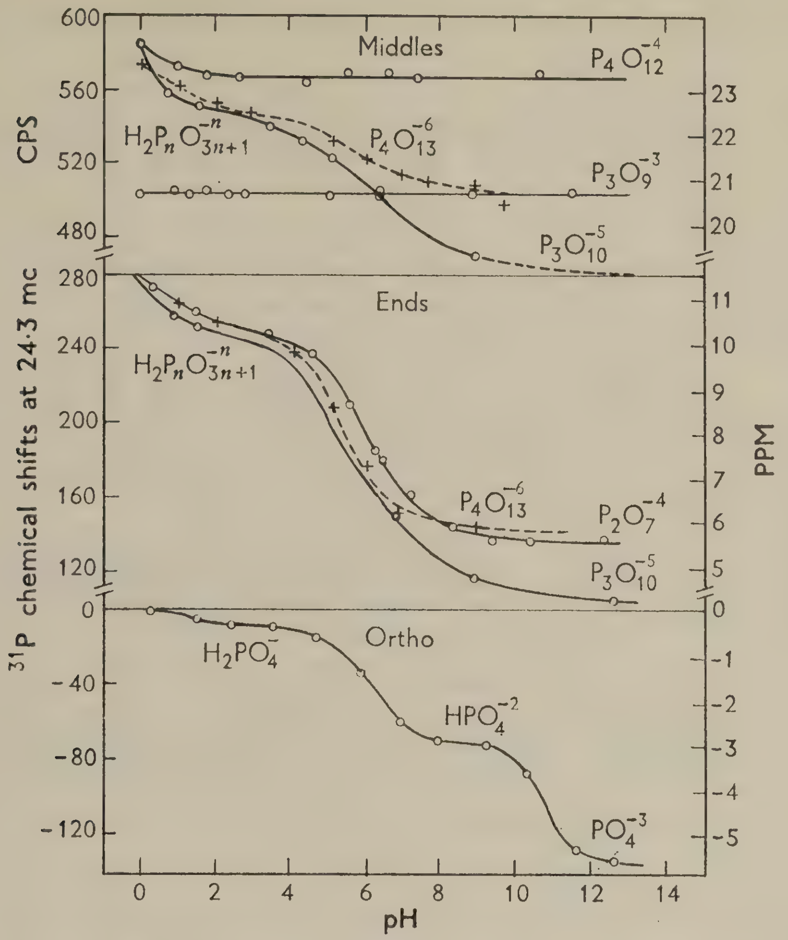


FIG. 12.—Change in $^{31}$P chemical shifts of ortho and condensed phosphates with pH

against pH, inflections appear in the curve (Fig. 12) at positions corresponding to $H_2PO_4^-$ and $HPO_4^=$.[739] The changes in shift are related to the formation of P–O–H bonds of some covalent character.[739]

The effect on the resonance of adding paramagnetic ions has been investigated.[1251] The line width was increased by a different amount by different ions, but no changes in chemical shifts were observed.

Simple crystals of crystalline fluorapatite have been studied by wide-line $^{19}$F and $^{31}$P nuclear magnetic resonance.[1252] The line shapes and second moments were compared with the theoretical calculations based on the crystal structure.

The $^1$H wide-line nuclear magnetic resonance spectrum of phosphomolybdic acid, $H_3PMo_{12}O_{40}$,$29H_2O$, has been studied.[1258] From the dependence of the line shape on temperature and from infra-red data the presence of the oxonium ion was deduced.

## PYROPHOSPHATES

The crystal structure of the isomorphous cubic pyrophosphates of silicon, titanium, zirconium, stannic tin, hafnium and uranium, having the general formula $MP_2O_7$, has been investigated.[547–8] The space group is reported as *Pa*3 and the lattice constants are given in Table XIV. It follows[547] from the choice of space group that the pyrophosphate ion must lie on a threefold axis, giving a P–O–P angle of 180°. It has recently been shown[717] that the linearity of this P–O–P group is not dependent on the choice of space group; the cubic cell and the assumption of a discrete pyrophosphate ion are sufficient to place the ion on a threefold axis. Reasonable agreement[547] between observed and calculated intensities was obtained for zirconium pyrophosphate with P–O (internal) = 1·56 A., P–O (external) = 1·52 A. (Owing to a numerical error in the original paper[547] the results of this work have been wrongly

*Table XIV.—Crystallographic Data on Pyrophosphates*

| Compound | Crystal system | Space group | Structure prototype | Unit cell dimensions | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | *a*<br>A. | *b*<br>A. | *c*<br>A. | *Z* | |
| $\alpha$-$Ba_2P_2O_7$ | Orthorhombic | — | — | 9·35 | 13·87 | 5·61 | | 553 |
| $\alpha$-$Ca_2P_2O_7$ | Orthorhombic | — | — | 8·44 | 12·52 | 5·26 | | 553 |
| $\beta$-$Ca_2P_2O_7$ | Tetragonal | $P4_1$ | | 6·684 | | 24·144 | 8 | 549, 1263 |
| $\alpha$-$Cu_2P_2O_7$ | Monoclinic | *C*2/*c*? | Similar to $\beta$-$Mg_2P_2O_7$ with doubled c | 6·876 | 8·113<br>$\beta$=109·54° | 9·162 | 4 | 1311<br>(see also 904) |
| $GeP_2O_7$ | Hexagonal | | | 8·00 | | 24·9 | 9 | 1265–6 |
| $HfP_2O_7$ | Cubic | *Pa*3 | $ZrP_2O_7$ | 8·18 | | | | 547 |
| $K_2H_2P_2O_7,\frac{1}{2}H_2O$ | Monoclinic | *C*2/*c* | | 17·92 | 7·01<br>$\beta$=120·7° | 14·27 | 8 | 549 |
| $KAlP_2O_7$ | Monoclinc | | | 7·31 | 9·74<br>$\beta$=122° 30′ | 9·09 | 4 | 1264 |
| $\beta$-$Mg_2P_2O_7$ | Monoclinic | *C*2/*m* | Thortveitite $Sc_2Si_2O_7$ | 6·49 | 8·28<br>$\beta$=104° 5′ | 4·51 | 2 | 905 |
| $Mn_2P_2O_7$ | Monoclinic | *C*2/*m* | $\beta$-$Mg_2P_2O_7$ | 6·63 | 8·58<br>$\beta$=102° 40′ | 4·54 | 2 | 903 |
| $(NH_4)_2H_2P_2O_7$ | Monoclinic | $P2_1/c$ | | 7·36 | 11·26<br>$\beta$=108·5° | 9·06 | 4 | 1310 |
| $(NH_4)_3HP_2O_7$ | Monoclinic | $P2_1/c$ | | 6·63 | 19·74<br>$\beta$=111·0° | 7·09 | 4 | 1310 |
| $(NH_4)_3HP_2O_7,H_2O$ | Triclinic | $P\bar{1}$ | | 9·13<br>115·4 | 6·33<br>77·2 | 9·96<br>109·2 | 2 | 1310 |
| $(NH_4)_4P_2O_7$ | Monoclinic | *C*2/*c* | | 11·77 | 6·51<br>$\beta$=104·7° | 13·63 | 4 | 1310 |
| $Na_4P_2O_7,10H_2O$ | Monoclinic | *I*2/*c* | | 17·93 | 6·96<br>$\beta$=118° 31′ | 14·85 | | 551 |
| | Monoclinic | *C*2/*c* | | 16·95 | 6·94<br>$\beta$=112° | 14·81 | 4 | 549 |
| | | *C*2/*c* | | 17·92 | 6·97<br>$\beta$=118° 30′ | 14·9 | 4 | 552 |
| $Na_2H_2P_2O_7,6H_2O$ | Monoclinic | *C*2/*c* | | 14·11 | 7·03<br>$\beta$=117·6° | 13·50 | 4 | 549 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $Na_3HP_2O_7,9H_2O$ | Monoclinic | $P2_1/a$ | | 8·59 | 31·65<br>$\beta = 113{\cdot}7°$ | 6·13 | 4 | 549 |
| $Nb_2O_5,2P_2O_5$ | Cubic | | $ZrP_2O_7$ | 8·073 | | | 2 | 1211 |
| $Sc_4P_2O_7$ | Tetragonal | $P4_22_1$ | | 10·17 | | 8·04 | 1 | 1279 |
| $SiP_2O_7$ | Cubic | $Pa3$ | $ZrP_2O_7$ | 7·46 | | | | 547 |
| $SnP_2O_7$ | Cubic | $Pa3$ | $ZrP_2O_7$ | 7·89 | | | | 547 |
| $\alpha$-$Sr_2P_2O_7$ | Orthorhombic | | | 8·87 | 13·27 | 5·39 | | 553 |
| $TiP_2O_7$ | Cubic | $Pa3$ | $ZrP_2O_7$ | 7·80 | | | | 547 |
| $UP_2O_7$ | Cubic | $Pa3$ | $ZrP_2O_7$ | 8·61 | | | | 548 |
| $WOP_2O_7$ | Monoclinic | $C2/m$ | | 15·170 | 5·162<br>$\beta = 102{\cdot}41°$ | 6·917 | | 648 |
| $\beta$-$Zn_2P_2O_7$ | Monoclinic | $C2/m$ | | 6·61 | 8·29<br>$\beta = 105{\cdot}4°$ | 4·51 | 2 | 1261–2 |
| $ZrP_2O_7$ | Cubic | $Pa3$ | | 8·20 | | | | 547 |
| | | | | 8·258 | | | | 554 |
| $2BaO,P_2O_5,B_2O_3$ | Hexagonal | | | 7·111 | | 13·977 | | 1209–10 |
| $2CaO,P_2O_5,B_2O_3$ | Hexagonal | | | 6·688 | | 13·234 | | 1209–10 |
| $2SrO,P_2O_5,B_2O_3$ | Hexagonal | | | 6·857 | | 13·657 | | 1209–10 |

quoted by some authors[565,716] as leading to a P–O–P angle of 152°.) A high-temperature form of zirconium pyrophosphate, also cubic, has been reported.[554] The linear P–O–P linkages in zirconium pyrophosphate and its isomorphs are unusual; such linkages have also been reported in $\beta$-$Mg_2P_2O_7$[905] and $Mn_2P_2O_7$[903] but other pyrophosphates which have been studied show non-linear P–O–P linkages. The crystal structure of $\beta$-$Mg_2P_2O_7$ has recently been refined[1260] and that of $\beta$-$Zn_2P_2O_7$ determined.[1261-2] In both structures the central oxygen atom of the pyrophosphate ion was found to have enhanced thermal motion in the plane perpendicular to the P–P vector. Evidently the P–O–P bond appears linear only because of the thermal averaging of the central atom position. Bond lengths are for $\beta$-$Mg_2P_2O_7$ P–O(–P) 1·557 (assuming POP = 180°), P–O 1·534, 1·542; for $\beta$-$Zn_2P_2O_7$ P–O(P) 1·569 (for POP = 180°), P–O 1·556, 1·554 A. It is not clear whether the thermal motion is real or due to statistical disorder and, if real, whether it is vibrational or rotational. A single-crystal *X*-ray study[1276] of germanium pyrophosphate has shown that the real cell ($a = 22{\cdot}854$ A.) is twenty-seven times that quoted in the early work.[547-8] Weak lines indicating the larger cell were observed on powder diffractometer traces of Ge, Sn, Pb, Ti, Zr, Hf, Th, U pyrophosphates. Evidently all the cubic pyrophosphates possess the big cell; values in Table XIV refer to the sub-cell. The symmetry requirement that all the P–O–P bonds be linear (or disordered) is relaxed in the larger cell. The crystal structure[1311] of $\alpha$-$Cu_2P_2O_7$ shows the pyrophosphate ion to have a twofold axis and a P–O–P bond angle of 157°. Like the compounds above the high-temperature ($\beta$) phase has a (pseudo) linear P–O–P bond. Diffuse streaks in the *X*-ray scattering pattern in the temperature range of the transition support a positional disordering of pyrophosphate ions.[1311] A preliminary report[549] of a possible linear P–O–P linkage in disodium pyrophosphate hexahydrate, $Na_2H_2P_2O_7,6H_2O$, has since been discounted.[550] In tetrasodium pyrophosphate hexahydrate, $Na_4P_2O_7,10H_2O$,[551] the P–O–P angle is 134°, the internal bonds 1·63 A., and the external bonds an average of 1·47 A. This structure has recently been refined[744] leading to bond lengths of $1{\cdot}61 \pm 0{\cdot}015$ and $1{\cdot}51 \pm 0{\cdot}015$ A., with a P–O–P angle of 133½°, and O–P–O angles of 113° (between external oxygen atoms) and 105° (between internal and external oxygen atoms). When viewed down the P–P vector, the two $-PO_3$ groups are staggered with respect to each other. The space group is stated to be I2/*c*; earlier reports[548,552] gave *C*2/*c*. The crystal structure[1263] of $\beta$-$Ca_2P_2O_7$ shows two independent pyrophosphate groups in an essentially eclipsed configuration. The POP angles are 131° and 138°, and the bond lengths: P–O(P) $1{\cdot}615 \pm 0{\cdot}017$, P–O $1{\cdot}518 \pm 0{\cdot}021$ A. Unit cell data and space groups (Table XIV) have been reported for several other pyrophosphates.[549,553,1211,1264-5] In the structure of tungsten oxypyrophosphate,[648] a P–O–P angle of 142° follows from presumed tetrahedral co-ordination of the phosphorus atoms, after some of the oxygen positions have been calculated from electron-density projections. The structure is built up of layers formed from fairly regular $WO_6$ octahedra, with oxygen atoms shared by coupling pyrophosphate groups. Each tungsten atom is in contact with five pyrophosphate groups, and each pyrophosphate group with five tungsten atoms. Each tungsten atom is also in contact with one oxygen atom which is not bonded to any other group. The layers are held together by Van der Waals forces and the crystals show pronounced layer cleavage.

The configuration of the pyrophosphate ion has also been investigated by spectroscopic means. The infra-red spectra of the $\alpha$ and $\beta$ forms of disodium pyrophosphate, $Na_2H_2P_2O_7$, have been studied in an unsuccessful attempt to determine the ionic symmetry in the crystals.[555] From the infra-red activity, in saturated solutions of tetrasodium and tetrapotassium pyrophosphate in normal and heavy water, of the totally symmetric P=O and P–O–P stretching vibrations of the pyrophosphate ion, which have been assigned[560] to Raman bands at 1018 and 718 cm.$^{-1}$ respectively, it has been concluded that the P–O–P linkage of the pyrophosphate ion is bent in solution.[556-7] In the infra-red (crystal, glass) and Raman (melt) spectra of tetrasodium pyrophosphate POP stretching vibrations were assigned[1267] at 714–730 (s) and 900–915 (as) cm.$^{-1}$, and $PO_3$ stretching vibrations at 1016–1030 (s) and 1100–

*Table XV.—References to Vibrational Spectra of Pyrophosphates*

| Compound | Infra-red (solid samples unless otherwise stated) | Raman |
|---|---|---|
| $Ag_4P_2O_7$ | 525–6, 559 | |
| $Ba_2P_2O_7$ | 525 | |
| $Ba_2P_2O_7$ | 1268 | |
| $Be_2P_2O_7$ | 1243 | |
| $Ca_2P_2O_7$ | 525, 1268 | |
| $CaH_2P_2O_7$ | 525 | |
| $Cd_2P_2O_7$ | 1268 | |
| $Co_2P_2O_7$ | 1268 | |
| $Cu_2P_2O_7$ | 1268 | |
| $GeP_2O_7$ | 1271, 1274 | |
| $GeO_2P_2O_5,2H_2O$ | 1274 | |
| $GeO_2P_2O_5,H_2O$ | 1274 | |
| $H_4P_2O_7$ | 561 ($CS_2$ solution) | 562–3 (liquid and glass) |
| $HfP_2O_7$ | 1270 | |
| $K_4P_2O_7$ | 525, 556–7 (solution in $H_2O,D_2O$), 561 | 521, 564–5 |
| $K_4P_2O_7,xH_2O$ | 526 | |
| $K_2H_2P_2O_7$ | 526 | 519 |
| $K_2D_2P_2O_7$ | 526 | |
| $K_2Na_2P_2O_7$ | — | 519 |
| $Li_4P_2O_7$ | 525 | |
| $Mg_2P_2O_7$ | 525 | |
| $\alpha$-$Mg_2P_2O_7$ | 1268, 1272 | |
| $\beta$-$Mg_2P_2O_7$ | 1268, 1272 | |
| $Mn_2P_2O_7$ | 1273 | |
| $(NH_4)_2H_2P_2O_7,xH_2O$ | 525 | |
| $Na_4P_2O_7$ | 525, 556–7 (solution in $H_2O,D_2O$), 560–1, 567, 665 | |
| $Na_4P_2O_7,10H_2O$ | 525, 561, 880 | |
| $Na_3HP_2O_7,H_2O$ | 561 | |
| $Na_3HP_2O_7,9H_2O$ | 561 | |
| $Na_2H_2P_2O_7$ | 525–6, 555, 561, 565–7 | |
| $NaH_3P_2O_7$ | 561 | |
| $Ni_2P_2O_7$ | 1245 | |
| $Ni(NH_4)_2P_2O_7$ | 1245 | |
| $NiNa_2P_2O_7$ | 1245 | |
| $Pb_2P_2O_7$ | 525, 1268, 1270 | |
| $SiP_2O_7$ | 558, 1270–1, 1275 | |
| $SnP_2O_7$ | 558, 1270 | |
| $Sr_2P_2O_7$ | 525, 1268 | |
| $TiP_2O_7$ | 558, 1270 | |
| $Tl_4P_2O_7$ | 526 | |
| $UP_2O_7$ | 1270 | |
| $Zn_2P_2O_7$ | 1268 | |
| $ZrP_2O_7$ | 558, 1270–1 1273 | 558 |

1150 (as) cm.$^{-1}$. Approximate force constants have been calculated[1268–9] for the pyrophosphate ion, although one set[1268] is based on the somewhat unlikely assignment of $\nu_s$(POP) at 909 cm.$^{-1}$. The calculations were based on a linear P–O–P bond and the results compared with data on a variety of crystalline phosphates. In the infra-red spectra of the cubic crystalline pyrophosphates, absorptions in the 1060–1125 and 500–675 cm.$^{-1}$ regions were interpreted as arising from stretching vibrations of an M–O–P group and as suggesting covalent bonding between the pyrophosphate groups and the metal atom.[558] It was argued that these compounds could be considered as double oxides, and that this might account for the linearity of the P–O–P group. However, the bands around 500 cm.$^{-1}$ attributed to M–O stretching have been assigned by other workers[1269] to bending motions of the pyrophosphate ion, the double oxide idea being rejected. Several workers[1270–1] have studied the spectra of the cubic pyrophosphates in some detail and shown them to be consistent with a linear P–O–P linkage. A variable-temperature infra-red study of magnesium pyrophosphate[1272] showed that in the low-temperature form the symmetry was not greater than $C_s$ or $C_2$, with a POP angle of not more than 150–160°. In the high temperature form the POP angle appears to be 180°, but the centrosymmetry is thought to be of a statistical nature. It was suggested that the potential energy curve for the POP vibration has two minima, and that the phase transition is explained by the thermal excitation of anionic inversion. Manganese pyrophosphate, also investigated,[1273] shows no such transition to a bent configuration at low temperatures. Other assignments of bands for the pyrophosphate ion are 900–915 cm.$^{-1}$ for the antisymmetrical P–O–P stretching vibration, 966–986 cm.$^{-1}$ for the out-of-phase symmetrical $PO_3$ stretching vibration, and 1122–1150 cm.$^{-1}$ for the unsymmetrical $PO_3$ stretching vibrations.[560] Other workers[559] suggested that a band at 930–950 cm.$^{-1}$ in the infra-red spectra of several pyrophosphates was characteristic of the pyrophosphate grouping and was probably the antisymmetric P–O–P stretching vibration. In another paper[561] on the infra-red spectra of alkali pyrophosphates the assignments of the P–O–P stretching vibrations were inverted, the symmetrical vibrations being placed at 917 cm.$^{-1}$ and the antisymmetrical ones at 700–740 cm.$^{-1}$ Stretching vibrations of the $PO_3$ groups were placed at 1144–1193 cm.$^{-1}$. The infra-red and Raman spectra of the dihydrogen pyrophosphate, $H_2P_2O_7^{2-}$, ion were determined[1320] from the study of aqueous solutions of $Na_2H_2P_2O_7$. Assignments, confirmed by deuterium exchange, included $\nu_{as}PO_2$ 1183, $\nu_sPO_2$ 1110, $\nu_{as}POP$ 910, and $\nu_{as}POP$ 715 cm.$^{-1}$ The broadness of the Raman bands below 750 cm.$^{-1}$ was attributed to rotational isomerism arising from hydroxyl groups on opposite phosphorus atoms. Pyrophosphates of which the spectra have been determined are given in Table XV. The infra-red spectra of large numbers of inorganic and organic pyrophosphates have been correlated, and a band in the 900–980 cm.$^{-1}$ region related to the presence of the pyrophosphate grouping.[215, 525, 559, 661–2, 777–8, 782]

The phosphorus nuclear magnetic resonance spectrum[171, 330, 568–9] of pyrophosphate ions shows a single peak, indicating equivalence of the phosphorus atoms. The chemical shift of tetrasodium pyrophosphate (relative to 85% orthophosphoric acid) is +6 p.p.m.[171, 330] Variation of this shift with pH has been investigated (Fig. 11) and related to the formation of P–O–H bonds of some covalent character.[739] The shifts for sodium and potassium acid pyrophosphates are +10 and +9 p.p.m. respectively.[171] An aqueous solution of pyrophosphoric acid has a shift of +10·6 p.p.m.[226] A rapidly rotating sample of pyrophosphoric acid gives a shift of +12 p.p.m.[971]

## TRIPHOSPHATES

The crystal structures of both forms of sodium triphosphate, $Na_5P_3O_{10}$, have been determined,[550, 574–5] and the results of the determinations on the low temperature phase II have recently been refined.[744] Both forms are monoclinic, space group $C2/c$, with a four-molecule cell, and in each case the triphosphate ions are slightly distorted from a symmetrical *trans* configuration, having axial symmetry and lying on twofold axes in the unit cell. In $Na_5P_3O_{10}$ II the sodium ions are co-ordinated by oxygen in a distorted octahedral arrangement; in $Na_5P_3O_{10}$ I two types of sodium have distorted octahedral co-ordination and a third type has fourfold co-ordination. Parameters of the two structures are given in Table XVI.

Sodium triphosphate hexahydrate, $Na_5P_3O_{10},6H_2O$, was said to be orthorhombic, with $a=7·53$, $b=10·23$, $c=9·83$ A.,[576] but more recent reports[1277–8] indicate it to be triclinic, with $a=9·799$, $b=10·30$, $c=7·652$ A., $\alpha=94·45°$, $\beta=92·20°$, $\gamma=90·99°$, $Z=2$,[1277] space group[1278] $P\bar{1}$. The crystal structure has been determined[1278] and confirms the large difference between the two types of P–O(–P) bond. The POP angle is 123·5°. Details have been published of the use of $X$-ray powder photographs for the

*Table XVI.—Structural Parameters of Sodium Triphosphates*

| Parameter | Phase I<br>Ref. 575 | Phase II<br>Ref. 550 | Phase II<br>Ref. 744 |
|---|---|---|---|
| Cell constants | | | |
| *a* | 9·61 A. | 16·00 A. | |
| *b* | 5·34 A. | 5·24 A. | |
| *c* | 19·73 A. | 11·25 A. | |
| *β* | 112° | 93° | |
| P–O bond lengths | | | |
| P–O–P inner | 1·62 A. | 1·61 A. | 1·61 ± 0·02 A. |
| P–O–P outer | 1·66 A. | 1·68 A. | 1·67 ± 0·02 A. |
| $PO_2$ | 1·52 A. | 1·49 A. | 1·49 ± 0·02 A. |
| $PO_3$ | 1·47 A. (av.) | 1·50 A. | 1·50 ± 0·02 A. |
| Angles | | | |
| (–O)–P–(O–) | 94° | 98° | 99° |
| P–O–P | 122° | 121° | 122° |
| $PO_2$ | | | 116° |
| $PO_3$ | | | 115° |
| $(O_3)PO$ | | | 103° |

analysis of commercial sodium triphosphates.[570, 748–50] Unit cell data for a series of ammonium triphosphates are listed on p. 1202.

Infra-red spectra have been reported[525, 560, 567, 577, 665] for sodium triphosphate phase I, phase II, and hexahydrate, and the spectra have been used for analytical purposes.[665] The infra-red spectrum of sodium triphosphate glass, and the Raman spectra of the melt[560] and solution,[760] have been determined. Assignments were made of a $PO_3$ symmetrical stretching vibration at 998 (Raman, very strong), or 1017 (infra-red, weak) $cm.^{-1}$, $PO_3$ antisymmetrical stretching vibrations at 1150 and 1085 $cm.^{-1}$ (Raman) or 1126, 1150, and 1215 $cm.^{-1}$ (infra-red, very strong), $PO_2$ antisymmetrical stretching vibration at 1215 $cm.^{-1}$ (infra-red), $PO_2$ symmetrical stretching vibration at 1112 $cm.^{-1}$ (Raman, strong), POP symmetrical stretching vibrations at 692–712 $cm.^{-1}$ (Raman and infra-red) and 760 $cm.^{-1}$ (infra-red only), and POP antisymmetrical stretching vibrations at 886 (Raman, weak), 888 (infra-red) $cm.^{-1}$ and 953 $cm.^{-1}$ (infra-red).[560] The infra-red spectra of potassium triphosphate,[525] silver triphosphate,[525–6] dizinc sodium triphosphate,[526] dizinc sodium triphosphate nonahydrate[525] and nickel trisodium triphosphate dodecahydrate[525, 1245] have been reported.

The phosphorus nuclear magnetic resonance spectrum of triphosphate ions[171, 330, 568–9, 663] shows separate peaks, corresponding to the end and middle groups, with relative intensities of two to one, and a doublet and triplet spin-spin splitting respectively, confirming the chain structure of the ion. The chemical shifts[171] are +4 p.p.m. for the end groups and +18 p.p.m. for the middle groups. The spin-spin splitting between the non-equivalent phosphorus nuclei is 16 cycles/sec.[171, 663] Changes in chemical shift with pH have recently[739] been observed for both end and middle groups (Fig. 11). These changes are attributed to the formation of P–O–H bonds of some covalent character. The change of shift with pH for middle groups is about half that for end groups, and this is taken as an indication that the hydrogen atoms spend some time on the middle groups as well as on the end groups. The lack of any P–O–H spin-spin coupling and the appearance of single phosphorus resonances are strong evidence for a rapid exchange of hydrogen atoms, so that only information on time-average location of these may be obtained.[739]

| Formula | Crystal system | Space group | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|
| | | | *a* | *b* | *c* | *Z* | |
| $(NH_4)_3H_2P_3O_{10}$ | Monoclinic | *P*2/*c* | 7·59 | 10·90<br>$\beta = 126{\cdot}1°$ | 8·78 | 2 | 1310 |
| $(NH_4)_3H_2P_3O_{10},H_2O$ | Monoclinic | *P*2$_1$/*c* | 7·31 | 8·08 | 21·73 | 4 | 1310 |
| $(NH_4)_4HP_3O_{10}$ | Monoclinic | *C*2/*c* | 14·24 | 7·47<br>$\beta$-109·5° | 12·59 | 4 | 1310 |
| $(NH_4)_9H(P_3O_{10})_2,2H_2O$ | Monoclinic | *C*2/*c* | 22·71 | 6·98 | 18·86 | 4 | 1310 |
| $(NH_4)_5P_3O_{10},H_2O$ | Triclinic | $P\bar{1}$ | 10·94 | 31·5<br>$\alpha \sim \beta \sim \gamma = 90 \pm 0{\cdot}2°$ | 6·43 | 6 | 1310 |

## LONGER-CHAIN PHOSPHATES

The infra-red spectrum of sodium tetraphosphate, $Na_6P_4O_{13}$, and the Raman spectrum of the melt have been determined.[560] The assignments made were very similar to those given above for the triphosphate.

The phosphorus nuclear magnetic resonance spectrum of tetraphosphate ions shows two peaks of equal intensity, one from the end groups at a chemical shift of +5 p.p.m., and one from the middle groups at a chemical shift of +18 p.p.m.[330] This distinction between end and middle group peaks is maintained throughout the whole range of polyphosphate chain lengths.[171, 330, 568–9] End group chemical shifts are between +6 and +9 p.p.m. Middle group shifts range from +18 p.p.m. in short chains to +21 p.p.m. in long chains. The intensity ratio of the two peaks provides a measure of the average chain length, and the method has been used for the analysis of polyphosphates.[787] The spectrum of tetraphosphate ions has recently[739] been analysed to give values of the spin-spin coupling constants of 19·7 c/s between inner and outer phosphorus nuclei, and 16·5 c/s between the inner nuclei. As with triphosphate ions, changes in pH cause changes in chemical shift, related to the formation of P–O–H bonds having some covalent character (Fig. 10). The changes for middle groups are smaller than with triphosphate ions.[739]

### Metaphosphates

The sparingly soluble crystalline alkali metal ‘metaphosphates’ of general formula $(MPO_3)_n$, typified by the varieties of Maddrell's salt, $(NaPO_3)_n$, and the sodium and potassium Kurrol salts, form fibrous crystals similar to those of asbestos. They are generally considered to contain long chains of $PO_3^-$ groups, and hence to be linear polyphosphates of high molecular weight, rather than true cyclic metaphosphates. The long chain structure has been confirmed for Maddrell's salt,[578] $(NaPO_3)_n$, and in detail for rubidium metaphosphate Kurrol salt,[579] $(RbPO_3)_n$, silver metaphosphate[906] $(AgPO_3)_n$, and sodium Kurrol salt type $\alpha$.[907] The unit cell of rubidium metaphosphate contains a portion of two different chains which spiral in opposite ways about the screw axes. The pattern repeats after two $PO_3$ units. The four-molecule cell is monoclinic, with $a = 12{\cdot}123$, $b = 4{\cdot}228$, $c = 6{\cdot}479$ A., $\beta = 96{\cdot}3°$, space group $P2_1/n$. Bond lengths were given as P–O (chain) 1·62 A., P–O (external) 1·47 and 1·45 A. This structure has more recently been refined[744]; the latest bond lengths are P–O (chain) $= 1{\cdot}616 \pm 0{\cdot}010$ A., P–O (external) $= 1{\cdot}488 \pm 0{\cdot}010$ A., with bond angles of O–P–O (chain) = 103°, O–P–O (external) = 120°, and P–O–P = 129°. The crystal structure of Maddrell's salt, $(NaPO_3)_n$ (II) is somewhat similar to that of rubidium metaphosphate, but is disordered.[1281] The pattern is repeated every three $PO_3$ units, being similar to $\beta$-wollastonite in this respect.[578] Silver metaphosphate, $(AgPO_3)_n$, and sodium Kurrol salt type $\alpha$ have similar structures with helically arranged chains of $PO_4$ tetrahedra parallel to the $b$ axis with four tetrahedra per repeat unit.[906–7] Each silver or sodium atom has five oxygen atom neighbours. Unit cell data (Table XVII) have been reported for several other sparingly soluble metaphosphates.

The Raman[584–5, 760] and infra-red[525, 567, 584] spectra of sodium and potassium Kurrol salts have been reported and assignments given.[584] Antisymmetrical $PO_2$ stretching vibrations were assigned in the infra-red at 1285 cm.$^{-1}$, and in Raman and infra-red at 1255–1270 cm.$^{-1}$, symmetrical $PO_2$ stretching vibrations in Raman and infra-red at 1140–1150 cm.$^{-1}$ and 1087–1108 cm.$^{-1}$, anti-symmetrical POP stretching vibrations in the infra-red at 980–1020 cm.$^{-1}$ and 860 cm.$^{-1}$, and symmetric P–O–P stretching vibrations at 677–730 cm.$^{-1}$ in the infra-red. Bending and rocking motions of the $PO_2$ groups were assigned to Raman bands at 514–534, 425–437, and 364–375 cm.$^{-1}$. Infra-red spectra of the two forms of Maddrell's salt, $[NaPO_3]_n$ II and III, have also been reported.[525, 567, 665] The infra-red spectrum (polarized radiation)[1291] of $(KPO_3)_x,K_2O$ showed fourteen bands between 650 and 1400 cm.$^{-1}$, indicating that interactions between $PO_3$ groups of different chains in the unit cell, as well as between neighbouring groups in the same chain, were important.

*Table XVII.—Unit Cell Data for Sparingly Soluble Metaphosphates*

| Salt | Unit cell data (A or degrees) | | | | | Space group | References |
|---|---|---|---|---|---|---|---|
| | *a* | *b* | *c* | *β* | *Z* | | |
| $(AgPO_3)_n$ | 11·86 | 6·06 | 7·31 | 93·5 | 8 | $P2_1/n$ | 907 |
| $[Ca(PO_3)_2]_n$ | 16·95 | 7·66 | 7·04 | 90 | 8 | $P2_1/a$ | 580 |
| $(CsPO_3)_n$ | 12·71 | 4·32 | 6·83 | 83 | 4 | $P2_1/n$ | 580 |
| $(KPO_3)_n$ Kurrol salt | 14·02 | 4·54 | 10·28 | 78·5 | 8 | $P2_1/a$ | 580–1, 1284 |
| $[Mo(PO_3)_3]_n$ | 10·76 | 19·48 | 9·55 | 97·6° | 12 | $I2/a$ or $I_2$ | 1289 |
| $[MoO_2(PO_3)_2]_n$ | 7·683 | 7·426 | 4·889 | — | 2 | $Pbcm$ | 1300 |
| $[(NH_4)PO_3]_n$ Kurrol salt | 19·95 | 6·91 | 6·28 | 98·5 | — | — | 154 |
| $[Na_2H(PO_3)_3]_n$ | 7·72<br>$\alpha=90·6°$ | 6·76<br>$\beta=92·4°$ | 7·11<br>$\gamma=103·1°$ | — | — | $P\bar{1}$ | 1285 |
| $(NaPO_3)_n$ II Maddrell salt | 7·93<br>$\alpha=89·1°$ | 7·00<br>$\beta=94·2°$ | 7·10<br>$\gamma=103·1°$ | — | 6 | — | 578, 1281 |
| $\alpha$-$(NaPO_3)_n$ Kurrol salt | 12·12 | 6·20 | 6·99 | 88 | 8 | $P2_1/n$ | 580, 906 |
| $\beta$-$(NaPO_3)_n$ Kurrol salt | { 11·37<br>(23·76 | 6·02<br>6·09 | 7·64<br>14·07 | 86<br>90·7 | 8<br>8) ? | $P2_1/n$<br>$B2_1/c$? | 580, 582<br>583 |
| $[Pb(PO_3)_2]_n$ | 7·30 | 7·96 | 17·31 | 89·5 | 8 | $P2_1/c$ | 581, 1282, 1288 |
| $(RbPO_3)_n$ | 12·12 | 4·23 | 6·48 | 85 | 4 | $P2_1/n$ | 580 |
| $[Ti(PO_3)_3]_n$ | 10·42* | 19·35 | 9·54 | — | 12 | $I2/a$ or $I_2$ | 1290 |

* *a* sin *β*.

### PHOSPHATE GLASSES

The Raman[584–5, 760] and infra-red[525, 567, 584] spectra of vitreous sodium polyphosphate (Graham's salt) have been reported. Assignments[584] are similar to those given for the Kurrol salts (above). The infra-red spectra of a wide range of phosphate and phosphate–fluoride glasses have been determined[647] over the region 2–15 microns. The cations present were sodium, potassium, calcium and lithium, and the composition of the glasses ranged from metaphosphate to pyrophosphate. The metaphosphate glasses of sodium, calcium and lithium show very similar spectra, suggesting structural similarities. The spectrum of potassium metaphosphate glass is very different, suggesting a different symmetry for the polyphosphate chain in the solid state. The addition of sodium fluoride or metallic oxides to the glasses causes radical changes in the spectra. The Raman spectrum of a glassy polyphosphoric acid obtained from the thermal dehydration of phosphoric acid or ammonium dihydrogen phosphate has been reported.[1280] Fourteen lines were reported, with three strong polarized lines at 686, 1151 and 1341 cm.$^{-1}$. Approximate stretching force constants were calculated.[1280] The cylindrical distribution function in oriented sodium metaphosphate glass fibres has been studied.[1283] In-chain and out-of-chain PO bond lengths of 1·62 and 1·46 A. respectively were found. It was suggested that long chains of $PO_4$ tetrahedra, along the fibre axis, were similar to those in $Rb(PO_3)_n$.

## CYCLIC PHOSPHATES

The phosphorus nuclear magnetic resonance spectra of tri- and tetrametaphosphates[171] show a single peak at about the same position as the middle group peak in chain phosphates, thereby confirming the cyclic structure. The shift range for different cyclic phosphates (sodium salts) has been quoted as 20·9 p.p.m. for the trimetaphosphate,[1192, 1322] 22·9 p.p.m. for the tetrametaphosphate,[1192] and 21·9 for the hexametaphosphate, all relative to 85% $H_3PO_4$.

The crystal structures of ammonium tetrametaphosphate, $(NH_4)_4P_4O_{12}$,[587–9, 744, 908] and of the monoclinic form of sodium tetrametaphosphate tetrahydrate, $Na_4P_4O_{12},4H_2O$,[590, 596, 751] have been determined. Ammonium tetrametaphosphate is orthorhombic, with $a=10\cdot42$, $b=10\cdot82$, $c=12\cdot78$ A. The unit cell contains four molecules, and has space group *Cmca*. Tetrametaphosphate ions, $P_4O_{12}{}^{4-}$, are stacked in a face-centered array, interleaved with layers of $NH_4$ cations. The tetrametaphosphate rings are nearly flat, with $C_{2h}$ symmetry. This structure has more recently been refined[744]; the latest bond lengths and angles are given in Fig. 13. Monoclinic sodium tetrametaphosphate tetrahydrate[751] has a bimolecular cell of dimensions $a=9\cdot667$, $b=12\cdot358$, $c=6\cdot170$ A., $\beta=92°\ 16'$, with space group $P2_1/a$. Sodium ions are co-ordinated by six oxygen atoms in an approximately octahedral configuration, and the tetrametaphosphate rings lie on centres of symmetry, also showing strong pseudo-$C_{2h}$ point symmetry, as in the ammonium salt. Bond lengths and angles are given in Fig. 13.

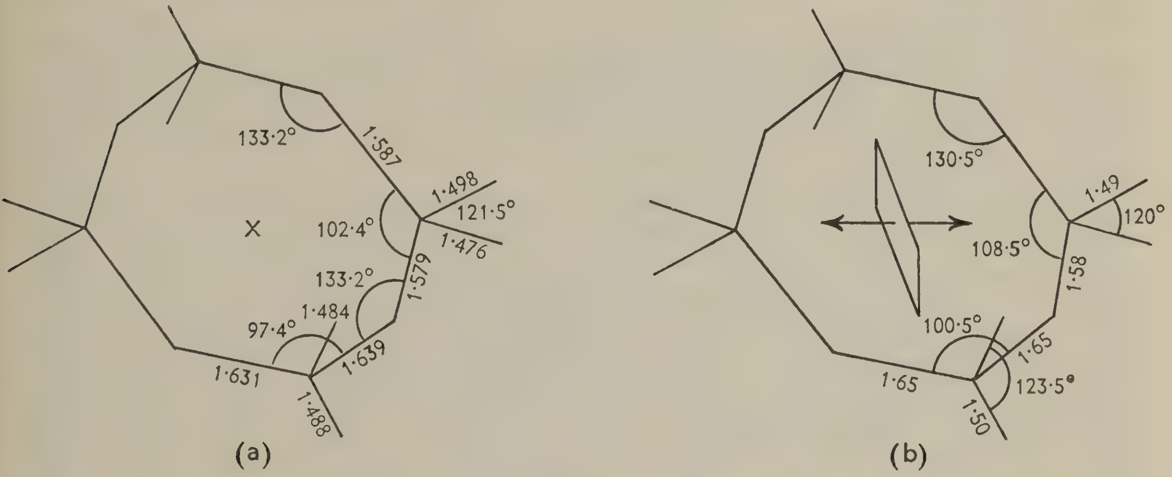


FIG. 13.—Bond lengths and angles of the tetrametaphosphate ions in (*a*) monoclinic sodium tetrametaphosphate tetrahydrate[751] (*b*) ammonium tetrametaphosphate[587–9, 744]

Recently the structures of triclinic sodium tetrametaphosphate tetrahydrate,[1293] sodium trimetaphosphate and its monohydrate[1294] have been determined. Triclinic $Na_4P_4O_{12},4H_2O$ has cell dimensions[1293] $a=6\cdot652$, $b=9\cdot579$, $c=6\cdot320$ A., $\alpha=103°\ 24'$, $\beta=106°\ 59'$, $\gamma=93°\ 17'$, space group $P\bar{1}$, $Z=1$. The tetrametaphosphate ring is on a centre of symmetry; there are some similarities between the monoclinic and triclinic structures, but the differences are too great to permit a transition between the two forms in the solid state.

Sodium trimetaphosphate and its monohydrate[668, 1294] have very similar structures. The anhydrous structure contains a hole which is large enough to accommodate the water molecule (but it cannot get in or out). In the hydrate the water fills this hole and there are some slight changes in the cell dimensions; this situation is thought to be unique. Both structures are orthorhombic with space group *Pmcn*, $Z=4$. The anhydrous salt has $a=7\cdot928$, $b=13\cdot214$, $c=7\cdot708$ A., and the monohydrate $a=8\cdot500$, $b=13\cdot189$, $c=7\cdot558$ A. Earlier cell data[591] on the anhydrous salt were not confirmed. The trimetaphosphate ions have a chair configuration lying on a mirror plane. The average ring angles are: O–P–O 101°, P–O–P 127°; the largest change on hydration is at the oxygen atom on the mirror plane, where the P–O–P angle changes from 128 to 122°. Bond lengths are as follows (values for the monohydrate in brackets): ring bonds 1·60 (1·61), 1·63 (1·63), 1·61 (1·63) A., exocyclic bonds 1·49 (1·51), 1·48 (1·47), 1·48 (1·49), 1·48 (1·47) A. Cell dimensions have also been reported[668] for the sesquihydrate, $Na_3P_3O_9,1{\cdot}5H_2O$ (orthorhombic, $a=11{\cdot}05$, $b=20{\cdot}70$, $c=8{\cdot}01$ A., $Z=8$, space group $A2_122$), and the trihydrate (tetragonal, $a=12{\cdot}86$, $c=12{\cdot}63$ A.). A second form of the monohydrate has been reported; it is tetragonal with a tetramolecular cell and $a=7{\cdot}99$, $c=13{\cdot}14$ A.[592]

The crystal structure of lithium dipotassium trimetaphosphate monohydrate has been determined.[1301] The cell is monoclinic, with $a=8{\cdot}669$, $b=14{\cdot}497$, $c=7{\cdot}634$ A., $\beta=99°\ 53'$, space group $P2_1/c$, $Z=4$. The trimetaphosphate ring has a chair form of pseudo-$C_{3v}$ symmetry. Average bond lengths are 1·61 A. for ring bonds, 1·49 A. for exocylic bonds, and average ring angles are 100·15° (O–P–O) and 128·9° (P–O–P).

Crystallographic data for some trimeta-arsenatophosphates, $Na_3(As,P)_3O_9$ have been reported.[1295] For As:P = 1:6, the unit cell is orthorhombic with $a=8{\cdot}04$, $b=13{\cdot}35$, $c=7{\cdot}82$ A., space group $P2_1cn$. For As:P = 1:12, it has $a=11{\cdot}31$, $b=20{\cdot}16$, $c=6{\cdot}94$ A., space group $Pmmb$ or $Pm2_1b$. For a ratio of As:P = 1:2·7, the cell is triclinic with $a=7{\cdot}97$, $b=7{\cdot}10$, $c=7{\cdot}14$ A., $\alpha=90{\cdot}1°$, $\beta=93{\cdot}2°$, $\gamma=103{\cdot}7°$, and the structure was determined.

The structure of sodium hexametaphosphate hexahydrate, $Na_6P_6O_{18},6H_2O$, has been determined.[1296] The structure is orthorhombic, space group $Ccma$, with $a=10{\cdot}58$, $b=18{\cdot}54$, $c=10{\cdot}48$ A. The anion $P_6O_{18}{}^{6-}$ has a cyclic chair-form structure, symmetry $C_{2h}$. Bond lengths are 1·60, 1·61, 1·62 A. in the ring, and 1·50, 1·48, 1·49, 1·49 A. exocyclic.

An approximate structure has been proposed for aluminium tetrametaphosphate.[586] The complicated cubic structure has a tetramolecular cell of side 13·63 A., and the space group is $I\bar{4}3d$. The tetrametaphosphate rings are puckered, with $S_4$ symmetry, and their outer oxygen atoms provide octahedral co-ordination for the aluminium ions.

A compound described as a sodium metaphosphate, $Na_2H_2P_4O_{12}$,[593] with a fibrous crystal habit, has been claimed to be an ultraphosphate, $Na_2P_4O_{11}$, on the basis of an *X*-ray investigation,[594] but more recent work[595] has cast doubt on this interpretation. One molecule was removed from the original formula to obtain agreement between calculated and observed densities, and the structure was said to comprise partly disordered chains, composed of tetrametaphosphate rings linked by the sharing of an oxygen atom between adjacent rings. Two forms are described; form I is monoclinic, $a=30{\cdot}7$, $b=6{\cdot}77$, $c=7{\cdot}12$ A., $\beta=94{\cdot}1°$, space group $P2_1/a$, while form II is monoclinic and pseudo-orthorhombic, with $a=18{\cdot}74$, $b=14{\cdot}79$, $c=7{\cdot}03$ A., $\beta=90{\cdot}0°$, space group $B2/a$ or $Ba$. The latest work[297–8] on the orthorhombic modification shows that the structure consists of $P_4O_{12}$ rings linked to chains, probably by hydrogen bonds. Each chain has two possible positions differing by $C/2$, producing the observed disorder.

It was concluded[602] from the Raman spectra of solutions of sodium, potassium and ammonium tetrametaphosphates that the tetrametaphosphate ion in solution has a puckered *trans*-configuration of $C_{2h}$ symmetry. Tentative assignments were made of antisymmetrical $PO_2$ stretching vibrations to bands at 1365 and 1248 cm.$^{-1}$; of symmetrical $PO_2$ stretching vibrations to bands at 1158 and 1114 cm.$^{-1}$; and of ring vibrations to bands at 1074, 1015, 897 and 813 cm.$^{-1}$. The Raman and infra-red spectra of crystalline tetrametaphosphates[603–4] have been interpreted as showing different symmetry for the anions; $S_4$ symmetry in aluminium tetrametaphosphate and $C_{2h}$ symmetry in ammonium tetrametaphosphate were suggested, confirming the *X*-ray results. The spectra of cupric tetrametaphosphate and magnesium tetrametaphosphate suggest different structures, the anion having $D_{2d}$ symmetry in each case. Suggested assignments were 1235–1314 cm.$^{-1}$ for $PO_2$ antisymmetrical stretching vibrations, 1093–1182 cm.$^{-1}$ for the symmetrical vibrations, and 880–1060 and 693–882 cm.$^{-1}$ for ring vibrations. Later work[1299] on the Raman (solution and solid) and infra-red (solid) spectra of sodium tetrametaphosphate suggested that the ring has a *trans*-$C_{2h}$ configuration in the solid as well as in solution.

The Raman spectra of solutions of sodium and potassium trimetaphosphate and trimetaphosphoric acid,[521, 565, 597–8, 600] and the infra-red spectra of sodium, potassium, silver and lead trimetaphosphate powders[525, 567, 584, 599, 665] have been determined. The Raman spectra were interpreted[598] as indicating a flat ring, with $D_{3h}$ symmetry for the trimetaphosphate ion in solution. Bands at 1158, 665, 634 and 398 or 356 cm.$^{-1}$ were assigned to $A_1'$-type vibrations, and bands at 1119, 1000 and 763 cm.$^{-1}$ to $E'$-type vibrations. Some of the more detailed assignments given in this paper have since been revised.[584, 601] From the infra-red spectrum of solid anhydrous sodium trimetaphosphate[584] it was concluded that the ion has $C_{3v}$ symmetry in this crystal. The $D_{3h}$ symmetry of the ion in solution was supported by the infra-red spectra of trimetaphosphate ions in solution in normal and heavy water[601]; in this paper the antisymmetrical $PO_2$ stretching vibrations were assigned at 1277 cm.$^{-1}$ (infra-red, $A_2''$) and 1243 cm.$^{-1}$ (Raman, $E''$), the corresponding symmetrical vibrations at 1158 cm.$^{-1}$ (Raman, $A_1'$) and 1098–1119 cm.$^{-1}$ (Raman and infra-red, $E'$), while ring vibrations were assigned at 1000–1015 cm.$^{-1}$ (Raman, infra-red), 763–783 cm.$^{-1}$ (Raman, infra-red), and 634 cm.$^{-1}$ (Raman). These assignments, particularly those for the ring vibrations, cannot be regarded as definitely established. In the same paper[601] the infra-red spectrum of crystalline sodium trimetaphosphate hexahydrate was given, and it was concluded that the ion in this crystal has $C_{3v}$ symmetry, as in the corresponding anhydrous salt. Later work,[1299] however, including polarization data on the solution, rejected the $D_{3h}$ symmetry in solution because of polarized bands (5 or 6) and the similarity to the crystal spectra. It was concluded that the symmetry was $C_{3v}$ both in the solid and in solution.

In addition to spectra contained in papers quoted above, the following infra-red spectra have been reported: sodium trimetaphosphate (anhydrous, monohydrate, hexahydrate), magnesium trimetaphosphate decahydrate, calcium sodium trimetaphosphate trihydrate, strontium trimetaphosphate heptahydrate, barium trimetaphosphate tetrahydrate, manganese trimetaphosphate undecahydrate, nickel trimetaphosphate,[1245] sodium tetrametaphosphate (normal and metastable forms, and monohydrate), silver tetrametaphosphate dihydrate,[525] silver trimetaphosphate,[525–6] silver tetrametaphosphate,[526] and magnesium tetrametaphosphate octahydrate, calcium tetrametaphosphate pentahydrate, strontium tetrametaphosphate pentahydrate, barium tetrametaphosphate tetrahydrate, lead tetrametaphosphate tetrahydrate, manganese tetrametaphosphate monohydrate, cupric tetrametaphosphate octahydrate, aluminium tetrametaphosphate[525] and nickel tetrametaphosphate.[1245] Both types of salt are generally characterized by strong absorption in the 510–580, 990–1020 and 1200–1280 cm.$^{-1}$ regions, with weaker absorptions around 750–820 cm.$^{-1}$, 1110 cm.$^{-1}$ and 1150 cm.$^{-1}$ [525, 660]

#### BRANCHED PHOSPHATES

The phosphorus nuclear magnetic resonance spectra of highly branched ultraphosphates heated to their softening point[171] show a broad peak at a chemical shift of +30–31 p.p.m. which is absent from unbranched material and may be assigned to the phosphorus atoms at branch points. Azeotropic phosphoric acid shows a similar peak at +34 p.p.m.[171]

## LOWER PHOSPHORUS OXYACIDS AND SALTS

### Phosphorous acid and phosphites

The crystal structure of phosphorous acid has been determined.[909] The unit cell is orthorhombic, with $a = 7{\cdot}27$, $b = 12{\cdot}06$, $c = 6{\cdot}85$ A., and eight molecules per cell, with space group $Pna2_1$. The $PO_3$ group has two P–O bonds of length 1·54 A. and one of length 1·47 A., supporting the expected structure $H_2(HPO_3)$. The molecules appear to be linked by two hydrogen bonds per molecule, as expected. The O–P–O angle between the two hydroxyl groups is 102 ± 3°, and the other two O–P–O angles are 113 ± 5° and 116 ± 3°.

The crystal structure of magnesium phosphite hexahydrate, $MgHPO_3,6H_2O$, has been determined.[605] The lattice is rhombohedral, with $a = 5{\cdot}96$ A. and $\alpha = 96° 24'$, space group *R*3. The structure is built up from discrete tetrahedral $[HPO_3]^{2-}$ and octahedral $Mg^{2+}(H_2O)_6$ groups, which are bound together by a continuous 3-dimensional system of hydrogen bonds. The phosphite ion has threefold symmetry and lies on a threefold axis of the unit cell. The P–H distance is 1·47 A., P–O = 1·51 A., and the angles H–P–O = 109°, O–P–O = 110°. The crystal structure of phosphorous acid has been reported.[658] The cell is orthorhombic, with $a = 7{\cdot}257$, $b = 12{\cdot}044$, $c = 6{\cdot}845$ A., space group $Pna2_1$, and eight molecules per cell. The P–H distance is close to 1·39 A.

Disodium phosphite pentahydrate, $Na_2HPO_3,5H_2O$, has an orthorhombic cell with $a = 6{\cdot}4$, $b = 7{\cdot}6$, $c = 9{\cdot}4$ A., and two molecules per cell.[910] The electron spin resonance spectrum of the $\gamma$-irradiated compound has been investigated[910] and shown to arise from the ionic radical $\cdot PO_3^{=}$. Strong hyperfine coupling with the phosphorus nucleus was observed, and the dependence of line splittings on the field direction indicated two magnetically distinct sites. This shows that the $HPO_3^{=}$ ion has a plane of symmetry perpendicular to the *b* axis. The spectrum of $\cdot PO_3^{=}$ is consistent with a pyramidal ion having O–P–O angles of 110°. This radical has also been observed in magnesium phosphite hexahydrate,[911] and in ammonium phosphorofluoridate,[1333] in which the principal values of the $^{31}P$ hyperfine interaction tensor for the radical were determined as 1822·3, 1419·7, 1408·6 Mc/s, in reasonable agreement with theoretical predictions.[1333]

The crystal structure of cupric phosphite dihydrate, $CuHPO_3,2H_2O$, has been determined.[1302] The structure is orthorhombic with $a = 6{\cdot}71$, $b = 9{\cdot}00$, $c = 7{\cdot}40$ A., $Z = 4$, space group $P2_12_12_1$. Zigzag chains of deformed octahedral $CuO_3(H_2O)_3$ groups are bound together by phosphite groups. Tin (II) phosphite, $SnHPO_3$, is orthorhombic,[1303] with $a = 4{\cdot}60$, $b = 6{\cdot}18$, $c = 12{\cdot}34$ A., $Z = 4$, space group *Pnnm* or *Pnn*2. Lead (II) nitrophosphite, $PbHPO_3,Pb(NO_3)_2$, is orthorhombic,[1304] with $a = 7{\cdot}22$, $b = 10{\cdot}46$, $c = 5{\cdot}42$ A., $Z = 2$, space group probably $Pmn2_1$.

The Raman spectra[518, 538, 597, 606–9] of phosphite ions in $H_3PO_3$, $KH_2PO_3$, $K_2HPO_3$, $Na_2HPO_3$, $NaH_2PO_3$ solutions and crystalline $H_3PO_3$ and $Na_2HPO_3$[606] have been obtained. Recent work on the Raman spectrum of $NaH_2PO_3$[916] has cast doubt on the published spectra of this and the monopotassium salt.[518, 597] Infra-red spectra have been reported for aqueous solutions of $Na_2HPO_3$ and $K_2HPO_3$,[566] for crystalline $Na_2HPO_3$, $BaHPO_3$, $CaHPO_3,H_2O$,[525, 610, 1306] $H_3PO_3$, $(NH_4)_2HPO_3$,[1306] $Na_2HPO_3,5H_2O$,[525, 610, 1307] $Li_2HPO_3,H_2O$, $SrHPO_3,H_2O$, $PbHPO_3$, $NiHPO_3,H_2O$,[525, 610] $NaH(HPO_3),2{\cdot}5H_2O$, $Na_2H_4(HPO_3)_3$, $NaH_3(HPO_3)_2$,[1307] and have also been observed in aqueous solutions of $NaH_2PO_3$.[878] The dibasic nature of the acid is confirmed by the general appearance of bands in the 2280–2430 cm.$^{-1}$ region, arising from P–H linkages. The Raman and infra-red spectra of mono- and disodium phosphite solutions[538, 878, 916] show clearly that the symmetry of the $HPO_3^{2-}$ ion is reduced in the former salt by the addition of a hydrogen atom to form $H_2PO_3^-$ ions. A symmetry of $C_{2v}$ has been suggested[610] from infra-red spectra for phosphite ions in various metallic salts, but it is not clear from the paper whether this refers to $HPO_3^{2-}$ or to $H_2PO_3^-$ ions. For the $HPO_3^{2-}$ ion in solution symmetry $C_{3v}$ has been suggested[538] and the latest infra-red work,[566] based on the spectra of crystalline barium phosphite and aqueous sodium and potassium phosphites, with earlier Raman work[538] confirms this and enables a full assignment of the spectra (Table XVIII) to be made. A normal co-ordinate calculation based on complete assignments of normal and deuterated compounds has been made[1306] using a simple valence force field. Results were $F_{PH} = 3{\cdot}331$, $F_{PO} = 6{\cdot}418$ millidynes/A. $C_s$ or $C_1$ symmetry was proposed for the phosphite groups in crystalline phosphorous acid.[1306] Figures of 3·0–3·5 millidynes/A. have also been suggested[1088] for $F_{PH}$ in phosphorous acid and different salts.

A band at 1744 cm.$^{-1}$ due to P–D stretching has been reported in the Raman spectrum of a strong solution of phosphorous acid in deuterium oxide. It is suggested that the deuterium exchange is evidence for the presence of small amounts of the tautomeric form $P(OH)_3$.[608] A similar band has been observed in the infra-red spectrum.[878]

*Table XVIII.—Spectra and Assignments*[566] *for Phosphite Ion,* $(HPO_3)^{2-}$

| Raman cm.$^{-1}$ ($Na_2HPO_3$ solution) | Infra-red cm.$^{-1}$ $K_2HPO_3$ solution | Infra-red cm.$^{-1}$ $BaHPO_3$ mull | Assignment |
|---|---|---|---|
| 459 m(d) | 465 m | 471 m<br>498 m | *E*, $PO_3$ degenerate deformation |
| 550? vw | 567 m | 591 m | $A_1$, $PO_3$ symmetrical deformation |
| 993 s (p) | 979 m | 977 m | $A_1$ $PO_3$ symmetrical stretch |
| 1032 m(d) | 1027 vw | 1006 w<br>1021 w | *E*, PH deformation |
| 1100? vw | 1085 vs | 1083 vs<br>1110 vs | *E*, $PO_3$ degenerate deformation |
| 2330 s(p) | 2315 m | 2410 m | $A_1$, PH stretch |

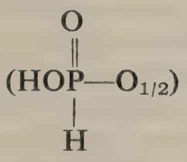
The far ultra-violet spectrum of phosphite ions in aqueous solution has been reported.[1318] The spectrum shows weak absorption above 200 mμ and a steeply rising absorption edge, attributed to a charge-transfer-to solvent transition, below 200 mμ.

The molar magnetic rotatory power (defined as $\rho M/d$, where $\rho$ is Verdet's constant, $M$ the molecular weight, and $d$ the density) of phosphite ions is $100 \times 10^{-2}$ min. of arc.[607, 611]

The phosphorus[110, 171, 225, 569, 634, 1308] and proton[225, 634, 1308] nuclear magnetic resonance spectra of phosphite ions are in agreement with the $HPO_3^{2-}$ structure. Strong phosphorus–proton spin-spin coupling is observed[171, 225, 634] indicating that the proton is directly bonded to the phosphorus. The phosphorus chemical shift lies between $-4$ and $-8$ p.p.m.[110, 171, 225] The spin-spin coupling constant $J_{P-H}$ was reported to be 707 c/s.[225, 634]

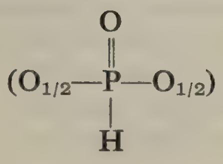
The effects of concentration, and of neutralization, on the NMR parameters of aqueous phosphorous acid have been investigated.[1250] The $^{31}P$ shift and the coupling constant varied from $-3{\cdot}9$ p.p.m. (relative to 85% $H_3PO_4$) and 664 c/s respectively at zero concentration to $-5{\cdot}8$ p.p.m. and 690 c/s at 10 molar. The effect of neutralization at constant phosphorus concentration was an increase in shift of about 1 p.p.m., to $-3{\cdot}3$ p.p.m., and a change in $J_{PH}$ from about 670 c/s to about 570 c/s. These changes were attributed to the association of protons with the anions. The effect of protonation of phosphorous acid has also been studied[1305] and followed by means of $J_{PH}$, which changes from 683 c/s to 806 c/s as the acid is protonated.

The $^{31}P$ NMR spectra of a series of polyphosphorous acids have been reported.[1309] Shift and coupling data were for end groups



$$(\mathrm{HO}\underset{\displaystyle\mathrm{H}}{\overset{\displaystyle\mathrm{O}}{\overset{\|}{\underset{|}{\mathrm{P}}}}}\text{—}\mathrm{O}_{1/2}) \quad \delta = +7{\cdot}4 \text{ p.p.m.}, \quad J_{PH} = 710 \text{ c/s}$$

for middle groups



$$(\mathrm{O}_{1/2}\text{—}\underset{\displaystyle\mathrm{H}}{\overset{\displaystyle\mathrm{O}}{\overset{\|}{\underset{|}{\mathrm{P}}}}}\text{—}\mathrm{O}_{1/2}) \quad \delta = +14, \quad J_{PH} = 760 \text{ c/s}$$

Data for the 'neso' group (orthophosphorous acid) $H_2.HPO_3$ were reported as $\delta = 3{\cdot}2$ p.p.m., $J_{PH} = 670$ c/s.

### Hypophosphites

The crystal structures of ammonium hypophosphite, $NH_4H_2PO_2$,[613] magnesium hypophosphite hexahydrate, $Mg(H_2PO_2)_2,6H_2O$,[614] and calcium hypophosphite, $Ca(H_2PO_2)_2$,[658] have been determined. Ammonium hypophosphite is orthorhombic, with $a = 7{\cdot}57$, $b = 11{\cdot}47$, $c = 3{\cdot}98$ A. The unit cell contains four molecules and the space group is *Cmna*. The structure is a distortion of the cæsium chloride arrangement. The hypophosphite ion was considered[613] as a distorted tetrahedron of $H_2PO_2^-$, with P–O = 1·52 A., and O–P–O = 121°. The position of the hydrogen atoms was not determined. Magnesium hypophosphite hexahydrate has a tetragonal cell, with $a = 10{\cdot}36$, $c = 20{\cdot}46$ A., containing eight molecules; a cell of half this size was reported earlier.[615] The space group is *I4/acd*. The P–O distance in the hypophosphite ion is 1·52 A., and the O–P–O angle 109°. Unit cell data have also been published[615] for cobaltous hypophosphite hexahydrate and the corresponding nickel salt, which are both isomorphous with magnesium hypophosphite hexahydrate. The tetragonal pseudo-cubic cells quoted, like that of the magnesium salt, may be half the true cells. The dimensions given are $a = c = 10{\cdot}22$ A. and 10·30 A. respectively for the cobalt and nickel salts. Calcium hypophosphite, which has been studied by both *X*-ray and neutron diffraction,[658] is monoclinic, with $a = 15{\cdot}08$, $b = 5{\cdot}66$, $c = 6{\cdot}73$ A., $\beta = 102{\cdot}8°$, space group *C*2/*c*. The P–O and P–H bond lengths are 1·505 A. and 1·39 A. respectively.

The electron spin resonance spectrum of $\gamma$-irradiated ammonium hypophosphite has been investigated.[912] The spectrum indicates that the ionic radical $H\dot{P}O_2^-$ is initially formed. There is strong hyperfine coupling to the phosphorus nucleus, and weaker isotropic coupling to the proton. The radical is irregular tetrahedral in shape with the unpaired electron occupying an $sp^3$ hybrid $\sigma$-orbital which is estimated to be 117 ± 5° from the direction of the P–H bond. There is evidence that the radical $H\dot{P}O_2^-$ reacts with an $H_2PO_2^-$ ion in an adjacent site along the *b* axis to form the species $O_2\dot{P}{-}PHO_2^{=}$. The angle between the P–P bond and the orbital of the unpaired electron is estimated to be 108 ± 5°.

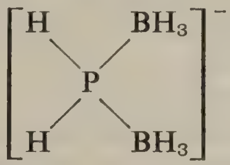
The Raman[518-9, 538, 565, 597, 609, 616, 912] spectra of hypophosphite ions in sodium and potassium hypophosphite solutions have been published. The infra-red spectra[525, 610, 912] of crystalline lithium, sodium, potassium, calcium, strontium, barium, lead and manganese hypophosphites, as well as of sodium hypophosphite monohydrate and magnesium hypophosphite hexahydrate, have been reported. The symmetry of hypophosphite ions in solution was suggested as $C_{2v}$ from an investigation of Raman spectra.[538] Later work[566] on the Raman and infra-red spectra of solutions of potassium hypophosphite, and the infra-red spectrum of an oriented film of potassium hypophosphite, using polarized radiation, has confirmed this. An assignment of the spectra was made, and the results with polarized radiation suggested that the crystal structure of potassium hypophosphite is similar to that of ammonium hypophosphite. A normal co-ordinate analysis has been carried out[617, 912, 1088] on the hypophosphite and deuterohypophosphite ions, using data from the normal and deuterated sodium, potassium and barium salts. The results confirm the conclusions of Reference 566. In another recent investigation[659] the infra-red spectra of thin films of hypophosphorous acid and the sodium, potassium, ammonium and calcium salts were obtained in a low-temperature cell. The infra-red spectra of the deuterated acid and salts, and the Raman spectrum of liquid hypophosphorous acid, were also obtained. From these data, complete and well-established assignments of the spectra of the hypophosphite and deuterohypophosphite ions were made on the basis of $C_{2v}$ symmetry. In solid potassium hypophosphite, $PH_2$ symmetric and antisymmetric stretching vibrations are at 2345 and 2320 cm.$^{-1}$ respectively, $PH_2$ deformation, wagging, twisting and rocking vibrations at 1172, 1082, 926 and

812 cm.$^{-1}$ respectively, and $PO_2$ antisymmetric stretching, symmetric stretching, and deformation vibrations at 1194, 1054 and 474 cm.$^{-1}$ respectively. The antisymmetric $PO_2$ stretching, symmetric $PO_2$ stretching, $PH_2$ rocking, and antisymmetric $PH_2$ stretching are, in order of decreasing strength, the strongest bands in the infra-red spectrum. The assignments were checked by the Teller–Redlich product rule. The infra-red spectrum of the calcium salt suggested $C_1$ or $C_2$ site symmetry for the hypophosphite ion in the crystal. The crystal structure[658] shows that the symmetry is actually $C_1$. A normal co-ordinate analysis of the hypophosphite ion was carried out, using a simple valence force field. Calculated and observed frequencies agreed to within 1·4%. The main force constants obtained were $F_{P-H} = 3{\cdot}077$ millidynes/Å., $F_{P-O} = 8{\cdot}133$ millidynes/Å.

In recent work the infra-red spectra of the hypophosphites of uranyl $[(UO_2)_2(H_2PO_2)_2,2H_2O]$, thorium $[Th(H_2PO_2)_4]$, ytterbium $[Yb(H_2PO_2)_3]$, thulium $[Tm(H_2PO_2)_3]$, samarium $[Sm(H_2PO_2)_3]$,[1316] lanthanum $[La(H_2PO_2)_3]$,[1316,1317] yttrium $[Y(H_2PO_2)_3]$ and scandium $[Sc(H_2PO_2)_3]$[1317] are reported. The Raman spectra of the first six compounds above are also reported.[1316] The spectra were similar to those of hypophosphites of monovalent cations.

The far ultra-violet spectrum of hypophosphite ions in aqueous solution has been reported.[1318] The spectrum shows weak absorption above 200 mμ and a steeply rising absorption edge, attributed to a charge-transfer-to solvent transition, below 200 mμ.

Some infra-red and spectral data for the ion:



analogous to hypophosphite, have been determined.[1319]

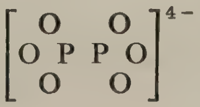
The phosphorus[110,171,225,569,612] and proton[225,634] nuclear magnetic resonance spectra of hypophosphite ions show spin-spin splitting of the phosphorus resonance into a triplet, confirming the $H_2PO_2^-$ structure. The phosphorus chemical shift is between −6 and −13 p.p.m.[171,225]; the spin-spin coupling constant $J_{P-H}$ has been reported as 593 cycles/sec.[225,634] and 561 cycles/sec.[612] The effects attributed to proton association of concentration and of neutralization on the NMR parameters of hypophosphorous acid have been investigated.[1250] The shift relative to 85% $H_3PO_4$ and the coupling constant changed from −10·5 p.p.m. and 547 c/s respectively at zero concentration to −12·2 p.p.m. and 566 c/s at 10 molar. The effect of neutralization at constant phosphorus concentration was an increase in shift of about 4 p.p.m., to −7·3 p.p.m., and a change in $J_{PH}$ from about 570 to 520 cycles. The effect of protonation of hypophosphorous acid in sulphuric acid has also been studied[1305]; the coupling constant increases from about 572 to about 674 c/s.

The possibility of a tautomeric form of hypophosphorous acid, containing trivalent phosphorus, has been suggested at various times and evidence for its existence has been claimed.[618] The concentration of any such form is evidently too low to be detected spectroscopically.

## OTHER OXYACIDS CONTAINING TWO PHOSPHORUS ATOMS

### Hypophosphates

Early work[620–1] on diammonium dihydrogen hypophosphate, $(NH_4)_2H_2P_2O_6$, used unit cell and space group considerations to show that the hypophosphate ion must have the symmetrical



$$\left[\begin{matrix} & O & & O & \\ O & P & & P & O \\ & O & & O & \end{matrix}\right]^{4-}$$

structure. A detailed structure determination[913] confirms this. The cell is orthorhombic, space group *Pccn*, with $a=7{\cdot}24$, $b=9{\cdot}36$, $c=11{\cdot}44$, $Z=4$. The hypophosphate ions lie on sites of twofold symmetry, but approximate to the symmetrical staggered ($D_{3d}$) configuration. The ammonium ions have fourfold co-ordination to the oxygen atoms of the hypophosphate ions. The bond lengths are P–P 2·17 A., P–O 1·50 A., P–O(H) 1·57 A., angles PPO = 106·7° (av.), OPO = 113·3°, 116·7°, 106·2°.

The electron spin resonance spectrum of $\gamma$-irradiated diammonium dihydrogen hypophosphate has been investigated[914] and shown to arise from the ionic radical $(O_2\dot{P}–PO_3)^{3-}$. On heating the crystal to about 120°C. the P–P bond of the trapped species breaks, the products being $PO_3^{=}$ and (presumably) $PO_2^{-}$.

The Raman spectra of solutions of dipotassium and monoammonium hypophosphate and of hypophosphoric acid have been reported.[622–3] In the earlier work,[622] the value of the P–P bond force constant of 2·34 millidynes/A. was obtained from the dipotassium salt, but the ion was regarded as $P_2O_6^{4-}$ instead of the more likely $H_2P_2O_6^{2-}$, and the agreement between calculated and observed frequencies was poor. In the later work[623] the ion was also regarded as $P_2O_6^{4-}$; the spectrum was said to be consistent with a staggered configuration, but there were discrepancies. Both studies, however, confirm the symmetrical $O_3PPO_3$ structure by the absence of a PH band. A recent investigation[915] gives three bands in the Raman spectrum of a solution of tetrapotassium hypophosphate, as well as the infra-red spectra of the aqueous and solid salt and of several other solid salts, mentioned below. The observed fundamentals were assigned, and assignments were also proposed for several of the unobserved fundamentals on the basis of combination bands. The spectra are regarded as supporting the staggered $D_{3d}$ configuration for the $P_2O_6^{4-}$ ion. The main assignments are as follow: 1064 (infra-red, $E_u$, degenerate P–O stretch), 1023 (Raman, $A_{1g}$, P–O breathing), 909 (infra-red, $A_{2u}$, symmetrical out of phase P–O stretch), 666 (Raman, $A_{1g}$, symmetrical $PO_3$ deformation, in phase), 568 (infra-red, $A_{2u}$, $PO_3$ symmetrical $PO_3$ deformation, out of phase) and 493 cm.$^{-1}$ (infra-red, $E_u$, $PO_3$ degenerate deformation).

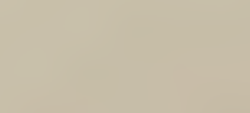
Infra-red spectra (of the solids) have been reported for tetrasodium hypophosphate, tetralithium hypophosphate mono- and heptahydrates, magnesium hypophosphate monohydrate, cerium hypophosphate monohydrate, sodium hexamminecobaltic hypophosphate tetrahydrate, thallous and silver hypophosphates,[915] barium and lead hypophosphates,[656, 915] sodium hypophosphate decahydrate, calcium hypophosphate dihydrate, strontium hypophosphate dihydrate, diammonium dihydrogen hypophosphate, disodium dihydrogen hypophosphate hydrate and dirubidium dihydrogen hypophosphate hydrate.[656] All show strong absorption in the 890–940 cm.$^{-1}$ and 1030–1135 cm.$^{-1}$ regions.[660]

The phosphorus nuclear magnetic resonance spectrum[171, 330, 569] of the hypophosphate ion shows a single peak, confirming the symmetrical structure. The chemical shift is $-9$ p.p.m.[171]

The far ultra-violet spectrum of hypophosphate ions in aqueous solution has been reported.[1318] The spectrum shows weak absorption above 200 m$\mu$ and a steeply rising absorption edge, attributed to a charge-transfer-to solvent transition, below 200 m$\mu$.

### Pyrophosphites

The Raman spectrum of sodium pyrophosphite,[609] $Na_2H_2P_2O_5$,[624–5] is as follows[625]: 335 (3), 449 (2), 469 (2), 529 (2), 559 (2), 720 (3), 917 (2), 1009 (6), 1033 (7), 1068 (3), 1107 (10), 1212 (3), 2417 (8). There is poor agreement between the data of Reference 625 and those of References 609 and 624. More recent work[916] supports the data given above. The spectrum of pyrophosphorous acid[625] has also been reported. The spectra are similar, and have been interpreted[625] as arising from a symmetrical anion

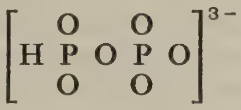


$$\left[\begin{array}{ccccc} & H & & H & \\ O & P & O & P & O \\ & O & & O & \end{array}\right]^{2-}$$

The phosphorus nuclear magnetic resonance spectra of sodium pyrophosphite[171, 569] and pyrophosphorous acid[626, 1321] have been determined. They show a symmetrical doublet arising from spin-spin splitting (by the protons) of the resonance from two chemically equivalent phosphorus atoms, confirming the above structure. The chemical shift is between +2·6 and +5 p.p.m., and the indirect spin-spin coupling constant $J_{P-H}$ is 685–780 c/s. The proton resonance also shows a doublet.[1308]

## Isohypophosphates

Although the Raman spectrum of sodium isohypophosphate, $Na_3HP_2O_6$, has been reported,[627] the main spectroscopic evidence for the structure of this anion comes from the phosphorus nuclear magnetic resonance spectrum.[171, 330] This shows resonances from two chemically non-equivalent phosphorus nuclei, one of which is split into a doublet by spin-spin interaction with the proton, while both phosphorus resonances are further split by spin-spin interaction between the two non-equivalent phosphorus nuclei. The P–H spin-spin splitting is 620 c/s, similar to that in phosphites; the P–P splitting (17 c/s) is similar to that across a P–O–P link in polyphosphates. The structure is therefore:

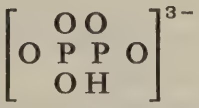


$$\left[\mathrm{H}\,\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\,\mathrm{O}\,\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\,\mathrm{O}\right]^{3-}$$

The chemical shifts are +1 p.p.m. ($PO_2H$ group) and +3 p.p.m. ($PO_3$ group), (relative to 85% orthophosphoric acid).

## Diphosphites

The Raman spectrum of molten sodium diphosphite dodecahydrate, $Na_3HP_2O_5$, $12H_2O$, has been determined.[628] Strong bands were assigned to PH and PP stretching vibrations at 2271 and 312 cm.$^{-1}$ respectively, and it was concluded that the anion has the structure:



$$\left[\mathrm{O}\,\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}\,\overset{\mathrm{O}}{\underset{\mathrm{H}}{\mathrm{P}}}\,\mathrm{O}\right]^{3-}$$

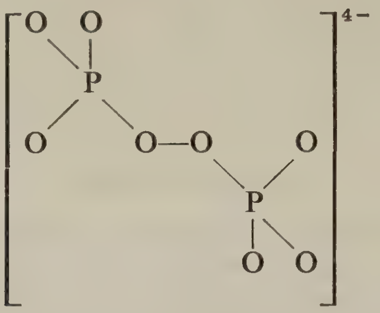
Weaker bands were observed at 427, 480, 504, 586, 615, 919, 950, 983, 1022, 1052, 1098 and 1114 cm.$^{-1}$

The phosphorus and hydrogen nuclear magnetic resonance spectra of the diphosphite ion[330] have established that the above structure is correct. The spectrum is that of two chemically non-equivalent phosphorus nuclei, both coupled by spin-spin interactions to a proton (an ABX system[629]). Analysis of the spectrum yielded the chemical shifts of +7·0 p.p.m. ($PO_3$ group), −22·8 ($PO_2H$ group), and the spin-spin couplings $J_{P_1P_2}=480$ c·s, $J_{P_1H}=444$ c/s, $J_{P_2H}=94$ c/s.

## OTHER OXYACIDS OF PHOSPHORUS

The crystal structure of the compound $Cs_6(PO_2)_6$ has been determined.[630] The structure is monoclinic, space group $P2_1/c$, with a two-molecule cell having $a=9{\cdot}47$, $b=9{\cdot}49$, $c=16{\cdot}05$ A., $\beta=110{\cdot}5°$. The oxygen positions were not determined accurately, but the phosphorus positions were determined sufficiently accurately to indicate that the anion is a puckered six-membered ring of phosphorus atoms, with attached oxygen atoms. The salt is hydrated, but the water molecules were not located. The ring lies on a twofold axis and has a chair configuration. Bond lengths are P–P = 2·18, 2·26, 2·16 A. (average 2·20 A.). Angles in the ring are 101·8, 104·5, 101·8°

The infra-red and Raman spectra of the alkali metal salts of peroxydiphosphoric acid, $H_4P_2O_8$, have been investigated.[557, 631] From considerations of the numbers of bands and their activity, structures with a linear P–O–O–P link were excluded, and it was concluded that the anion had the symmetrical *trans*-configuration:



with symmetry probably $C_2$ or $C_{2h}$. Suggested assignments were as follows: antisymmetric $PO_3$ stretching vibrations at 1132, 1159 and 1196 cm.$^{-1}$ in the infra-red, symmetric $PO_3$ stretching vibrations at 1008, 1101, 1125 cm.$^{-1}$ in the Raman, antisymmetric P–O–O–P stretching at 980–1005 cm.$^{-1}$ in the infra-red, symmetric P–O–O–P stretching at 784 cm.$^{-1}$ in the Raman, and symmetric O–O stretching at 890 cm.$^{-1}$ in the Raman spectrum. The infra-red spectra (as powders) of lithium, sodium, potassium, calcium, strontium and barium peroxydiphosphates, all with unknown amounts of water of crystallization, have been reported.[656,660] They show strong absorption in the 970–1000 and 1070–1200 cm.$^{-1}$ regions.

## Phosphorothioates

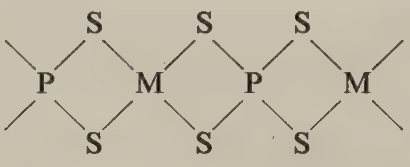
Cuprous phosphorotetrathioate, $Cu_3PS_4$, is orthorhombic, space group $Pmn2_1$, with $a = 6{\cdot}46$, $b = 7{\cdot}43$, $c = 6{\cdot}18$ A., $Z = 2$.[632] The data indicate the presence of tetrahedral $PS_4^{3-}$ ions.

Unit cell data for some sodium and potassium phosphorothioates have been reported[633,1324–5] and are given in Table XIX.

The average P–S bond length in potassium phosphorotetrathioate is 2·045 A.[1325]

The space-group possibilities for trisodium phosphorothioate require the anion to have at least threefold symmetry. In the remaining salts special symmetry is not imposed by space group considerations.

Aluminium[1326] and boron[1327] phosphorotetrathioates both have structures consisting of infinite chains of the form:



The aluminium salt[1326] is isostructural with silicon disulphide, and has an orthorhombic cell, with $a = 5{\cdot}61$, $b = 5{\cdot}67$, $c = 9{\cdot}05$ A., space group $P_{222}$. The boron salt has a high-temperature monoclinic form, with $a = 10{\cdot}38$, $b = 6{\cdot}05$, $c = 6{\cdot}69$ A., $\beta = 75°$, and a low-temperature orthorhombic form, with $a = 5{\cdot}60$, $b = 5{\cdot}25$, $c = 9{\cdot}04$. Average bond lengths were Al–S and P–S = 2·1 A. in the aluminium salt, and B–S = 1·89, P–S = 2·16 in the orthorhombic boron salt.

The Raman spectrum of trisodium phosphoromonothioate in aqueous solution and as the crystalline dodecahydrate, and the Raman[918] and infra-red[918,1328] spectra of the dodecahydrate and the anhydrous salt, have been reported. Symmetrical and degenerate stretching vibrations of the $PO_3$ group were assigned at 961 and 1037 cm.$^{-1}$ respectively, with bending modes of this group at 519 ($E$) and 610 ($A_1$) cm.$^{-1}$ The P–S stretching vibration was assigned at 436 cm.$^{-1}$ A normal co-ordinate analysis was carried out and stretching force constants $F_{P-O} = 5{\cdot}91$ millidynes/A. and $F_{P-S} = 2{\cdot}86$ millidynes/A. were obtained.[918] Spectra have also been reported for

*Table XIX.—Unit Cell Data for Phosphorothioates*

| Compound | Crystal system | Space group | Unit cell data (dimensions in A.) | | | | References |
|---|---|---|---|---|---|---|---|
| | | | *a* | *b* | *c* | *Z* | |
| Trisodium phosphorothioate<br>$Na_3PSO_3,12H_2O$ | Rhombohedral | $R\bar{3}m$ or $R32$ or $R3m$ | 12·58<br>$\alpha = 42·3°$ | | | 2 | 633 |
| Trisodium phosphorodithioate<br>$Na_3PS_2O_2,11H_2O$ | Orthorhombic | *Pnma* or $Pn2_1a$ | 12·51 | 13·94 | 9·48 | 4 | 633 |
| Trisodium phosphorotrithioate<br>$Na_3PS_3O,H_2O$ | Orthorhombic | — | 12·40 | 14·0 | 9·02 | 4 | 1324 |
| $Na_3PS_3O,11H_2O$ | Orthorhombic | *Pnma* or $Pn2_1a$ | 12·60 | 14·02 | 9·33 | 4 | 633 |
| Trisodium phosphorotetrathioate<br>$Na_3PS_4,8H_2O$ I | Monoclinic | $P2_1/c$ | 14·7 | 7·09<br>$\beta = 92°$ | 14·15 | 4 | 633 |
| $Na_3PS_4,8H_2O$ II | Monoclinic | $P2_1/c$ | 13·62 | 12·83<br>$\beta = 104°$ | 8·69 | 4 | 633 |
| Tripotassium phosphorotetrathioate<br>$K_3PS_4$ | Orthorhombic | *Pnma* | 9·10 | 10·51 | 9·01 | 4 | 1325 |

disodium phosphoromonothioate pentahydrate,[1328-9] diammonium phosphoromonothioate[1329] (infra-red) and disodium phosphoromonothioate in aqueous solution (Raman).

The infra-red spectra of phosphorotetrathioates show strong absorption in the 520–575 cm.$^{-1}$ region.[660] The infra-red spectra (as powders) of sodium phosphoromonothioate decahydrate, $Na_3PSO_3,10H_2O$, sodium calcium phosphoromonothioate octahydrate, sodium strontium phosphoromonothioate octahydrate, sodium barium phosphoromonothioate octahydrate and cobaltous, nickel and lead phosphoromonothioates, have been reported.[656] These salts show strong absorption in the 540–580 and 1010–1120 cm.$^{-1}$ regions.[656, 660]

The phosphorus nuclear magnetic resonance spectra of solutions of the various trisodium phosphorothioates in 3% sodium sulphide solution have been reported.[832, 917] The phosphorus chemical shifts, relative to 85% orthophosphoric acid, are as follow: $Na_3PS_4$, −87·5 p.p.m.; $Na_3POS_3$, −86·5 p.p.m.; $Na_3PO_2S_2$, −61·9 p.p.m.; $Na_3PO_3S$, −33·8 p.p.m.

## Phosphorofluoridates

The crystal structure of potassium phosphorodifluoridate, $KPO_2F_2$, has been determined.[1330] The cell is orthorhombic, with $a = 8{\cdot}03_9$, $b = 6{\cdot}20_5$, $c = 7{\cdot}63_5$ A., $Z = 4$, space group *Pnma*. Dimensions of the $PO_2F_2^-$ ion are as follow: P–O 1·470 A., P–F 1·575 A., FPF 97·1°, OPO 122·4°. Lead phosphorofluoridate, $PbPO_3F$, is orthorhombic,[1389] with $a = 6{\cdot}951$, $b = 8{\cdot}521$, $c = 5{\cdot}470$ A., $Z = 4$, space group *Pbnm* or *Pna*$2_1$, and is probably isostructural with lead sulphate.

The fluorine nuclear magnetic resonance spectra of phosphorofluoridic acid, $FPO(OH)_2$, phosphorodifluoridic acid, $F_2PO(OH)$[225, 634-5] and aqueous sodium phosphorofluoridate, $Na_2PO_3F$,[225] with the phosphorus spectra of phosphorodifluoridic acid,[110, 225] have been reported. Data have also been given[635] for a new phosphorus- and fluorine-containing species believed to be a phosphorofluoridate end group, $HO(O)P(F)O\frac{1}{2}$–. Chemical shift and spin-spin coupling data are given below:

| Compound | Phosphorus chemical shift (rel. to 85% $H_3PO_4$) p.p.m. | Fluorine chemical shift (rel. to $CF_3.COOH$) p.p.m. | $J_{P-F}$ c/s |
|---|---|---|---|
| $FPO(OH)_2$ | — | −2·5 | 954 |
| $F_2PO(OH)$ | 20·1 | 9·0 | 981 |
| $Na_2PO_3F$ aq. | — | 26·8 | 781 |
| $HO(O)P(F)O\frac{1}{2}$– (?) | 25·0 | −5·0 | 944 |

$^{31}P$ NMR data have also been reported[1331] for ammonium phosphorothiofluoridate, $(NH_4)_2PO_2SF$, and ammonium phosphorothiodifluoridate, $NH_4POSF_2$. Data (85% $H_3PO_4$ as standard) were as follows: $(NH_4)_2PO_2SF$ (aq.), $\delta_P = -43{\cdot}9$ p.p.m., $J_{PF} = 980$ c/s; $NH_4POSF_2$, $\delta_P = -47{\cdot}1$ p.p.m., $J_{PF} = 1120$ c/s. Spectra (NMR and infra-red) have been determined[1332] for various salts containing phosphorodithiodifluoridate $PS_2F_2^-$, pyrophosphoropentathiodifluoridate $S_2FPSPS_2F^{2-}$, and bis-phosphorotrithiofluoridate $FS_2PSSPS_2F^{2-}$, but the only data to have been reported[1332] are as follow: (ref. $CFCl_3$, $H_3PO_4$) $PS_2F_2^-$, $\delta_F = +2{\cdot}3$, $\delta_P = -118$ p.p.m., $J_{PF} = 1149$ c/s. $S_2FPSPS_2F^{2-}$, $J_{PF} = 1160$ c/s, $S_2FPSSPFS_2^{2-}$, $\delta_F = -7{\cdot}4$ p.p.m., $J_{PF} = 1170$ c/s.

The Raman spectra of molten potassium phosphorodifluoridate and a mixed sodium potassium phosphoromonofluoridate, as well as the infra-red spectra of crystalline potassium phosphoromono- and difluoridates, have been reported.[838] In the phosphoromonofluoridate, symmetrical and degenerate stretching vibrations of the $PO_3$ group were assigned at 998–1008 and 1120–1170 cm.$^{-1}$ respectively, with the P–F stretching vibration at 698–705 cm.$^{-1}$ and deformations of the $PO_3$ group in the 500 cm.$^{-1}$ region. In the phosphorodifluoridate, symmetric and antisymmetric vibrations of the $PO_2$ group were assigned at 1145 and 1290–1311 cm.$^{-1}$ respectively, with the corresponding vibrations of the $PF_2$ group at 824–834 and 857 cm.$^{-1}$ Stretching force constants of the PF and PO bonds were estimated as 3·8 and 7·3 millidynes/A. respectively in the phosphoromonofluoridate and 4·9 and 9·4 millidynes/A. in the phosphorodifluoridate.[838]

In a series of phosphorofluoridates including sodium and potassium phosphorodifluoridates and pyrophosphorodifluoridates, the symmetrical and antisymmetrical $PO_2$ stretching vibrations were assigned[1334] (inorganic derivatives only) in the ranges 1107–1166 and 1298–1323 cm.$^{-1}$ respectively. In phosphorodifluoridic acid, $F_2POOH$, the infra-red spectrum of the monomeric species has been determined[1335] from the spectrum of the superheated vapour. The PO frequencies are 1332 (assoc.), 1393 (free) cm.$^{-1}$ and the symmetric and asymmetric $PF_2$ stretching frequencies 881 (assoc.), 865/873 (free) cm.$^{-1}$, and 983 (assoc.), 956/967 (free) cm.$^{-1}$ respectively.[1335]

The infra-red spectra of ammonium phosphorodifluoridate, ammonium phosphoromonofluoridate monohydrate, calcium and strontium phosphoromonofluoridates (both with unknown water of crystallization), barium and lead phosphoromonofluoridates,[656] and sodium, potassium and silver phosphoromonofluoridates[526, 656] have been reported. The characteristic absorptions due to P–F stretching vibrations occur in the 720–835 cm.$^{-1}$ region.[656] Other strong absorptions occur in the 1090–1175 cm.$^{-1}$ region.[660] Infra-red spectra have also been reported for a series of phosphoromonofluoridate hydrates, as follows: $CdPO_3F,8H_2O$, $MnPO_3F,4H_2O$, $NiPO_3F,7H_2O$, $Cr_2(PO_3F)_3,18H_2O$, $Fe_2(PO_3F)_3,12H_2O$[1336] (all these hydrates were stated[1336] to be isomorphous with the corresponding sulphates), and for series of $NaPO_3$–NaF glasses of Na:P ratios between 1·28 and 1·5.[1337]

In the infra-red spectrum of phosphorothiodifluoridate ion, $SOPF_2^-$ (tetraethylammonium salt) the PO and PS stretching vibrations were assigned[1334] at 1218 and 658 cm.$^{-1}$ respectively. In a series of alkyl ammonium, phosphonium, and arsenium salts in this anion, the PO vibration was assigned[1338] in the range 1240–1247 cm.$^{-1}$ with the PS vibration at 645 cm.$^{-1}$, and $PF_2$ vibrations at 814–822 cm.$^{-1}$ (as) and 797–807 cm.$^{-1}$ (s).

## Phosphorochloridates

The phosphorus nuclear magnetic resonance spectrum of a system of phosphorochloridic acids has been investigated.[919] Phosphorodichloridic acid, $(HO)Cl_2PO$, has a chemical shift of $-9{\cdot}5$ to $-10{\cdot}5$ p.p.m. (relative to 85% orthophosphoric acid). Peaks at chemical shifts of $-18{\cdot}2$ p.p.m. and $-13{\cdot}0$ p.p.m. were tentatively assigned to phosphoromonochloridic acid, $(HO)_2ClPO$, and to the monochlorphosphate end group, $(HO)ClP(O)O_{\frac{1}{2}}$–, respectively.

NMR data have been reported[1339] for the phosphorothiochlorofluoridate ion $SPOClF^-$ (tetraphenylphosphonium salt). The $^{19}F$ chemical shift ($CCl_3F$ ref.) was $+43{\cdot}6$ p.p.m., and the coupling constant $J_{PF}$ was 1056 c/s.

The Raman spectrum of phosphorodichloridic acid, $(HO)Cl_2PO$, has been reported.[1340] Assignments included 1249 ($\nu$PO), 595 ($\nu_{as}PCl_2$) and 554 cm.$^{-1}$ ($\nu_s PCl_2$). In the infra-red spectra of a series of phosphorodichloridate salts, vibrations were assigned[1341] as follows: $\nu_{as}PO_2$, 1205–1259; $\nu_s PO_2$ 1082–1147, $\nu_{as}PCl_2$ 608–708, $\nu_s PCl_2$ 569–590 cm.$^{-1}$ In the salts $M(O_2PCl_2)_3$ (M = Al, Ga, In, Fe) polymeric structures with oxygen bridges were proposed on the basis of the infra-red spectra, with bands at 481–542 and 190–337 cm.$^{-1}$ attributed to vibrations of the $MO_6$ octahedra. In the beryllium salt, $Be(O_2PCl_2)_2$, these bands are absent, evidently because of the ionic nature of the salt.

The infra-red spectra of a series of phosphonium and arsenium phosphorothiodichloridates, $X^+Cl_2POS^-$, and phosphorothiochlorofluoridates, $X^+FClPOS^-$, have been reported.[1339] Assignments included the following: $\nu$PO 1210–1215 ($Cl_2POS^-$), 1228–30 ($FClPOS^-$); $\nu$PS 645–7 ($Cl_2POS^-$), 638–640 ($FClPOS^-$); $\nu_{as}PCl_2$ 462–5, $\nu_s PCl_2$ 437–8 ($Cl_2POS^-$); $\nu$PF 792–5, $\nu$PCl 477–483 ($FClPOS^-$) cm.$^{-1}$

## PHOSPHORUS–NITROGEN COMPOUNDS

### Ionized Phosphorus–Nitrogen Compounds

The crystal structure of sodium monoamidophosphate, $NaHPO_3.NH_2$, has been determined.[657] The structure is hexagonal, with $a = 5{\cdot}773$ and $c = 6{\cdot}031$ A., $Z = 2$, space group $Pb_3$. The amidophosphate anion is a zwitterion similar to the sulphamate ion, and the formula can be written $Na^+[NH_3{}^+PO_3{}^-]^-$. Each nitrogen atom of the anion is linked by three equivalent hydrogen bonds to the oxygen atoms of three other anions, as shown in Fig. 14.

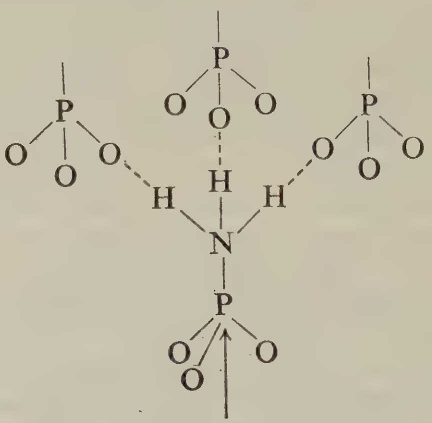


FIG. 14.—Detail of structure of sodium monoamidophosphate

The P–N bond lies on a threefold axis. Each sodium atom is surrounded by a distorted octahedron of oxygen atoms at distances of 2·39 or 2·43 A. This structure has recently been refined[744]; the bond lengths from this refinement are P–N = 1·769 ± 0·019 A., P–O = 1·522 ± ·011 A., and the angles, O–P–O = 114°, N–P–O = 103°. The N–H–O distance is 2·84 A.[657]

The infra-red spectra of dipotassium monoamidophosphate and barium diamidophosphate have been reported, as have the spectra of the thermal decomposition products of these salts, of empirical composition approximately $K_4P_2O_6NH$, $K_6P_3O_9N$ and $Ba(PO_2NH)_2$.[1343]

The infra-red spectra of a number of diamidophosphoromonothioates, $M^+POS(NH_2)^-$, have been reported.[1344] These included the sodium salt, sodium salt dihydrate (Raman spectrum also), calcium and strontium salts (aq. solution), and barium salt dihydrate (Raman also). Assignments made included $\nu$PO 1105–1160, $\nu_{as}PN_2$ 770–845, $\nu_s PN_2$ 778–825, $\nu$PS 480–533 cm.$^{-1}$

The infra-red spectra (KBr discs, aqueous solutions) of monoamidophosphoric acid and its monosodium,[920, 1342] monopotassium, monosilver and monobarium salts, as well as the disodium salt, have been reported, and assignments proposed[920] which differ from earlier assignments[667] by the same author. The $A_1$ and $E$ bending vibrations and the rocking vibration of the $NH_3{}^+$ groups in the zwitterions $[PO_3{}^-NH_3{}^+]^-$ are assigned around 1480, 1610 and 1020 cm.$^{-1}$ respectively, with the $A_1$ and $E$ stretching vibrations of the $PO_3{}^-$ group around 993 and 1165 cm.$^{-1}$ [920] and the P–N stretching vibration around 710 cm.$^{-1}$ [667, 920] In the disodium salt, $[Na^+]_2[PO_3NH_2]^{2-}$, the $NH_2$ bending and rocking vibrations are assigned at 1610 and 1078 cm.$^{-1}$ respectively, the symmetric and antisymmetric $PO_3$ stretching vibrations at 980 and 1141/1188 cm.$^{-1}$,[920] and the PN stretching vibration at 810 cm.$^{-1}$ [667, 920] The difference between the P–N stretching frequencies is regarded[920] as indicating stronger P–N bonds in the $PNH_3{}^+$ group than in the $PNH_2$ group. Other workers have suggested[660–2] that the P–N group absorbs in the region 680–750 cm.$^{-1}$; however, some authors[526] regard the major part of the absorption in the 650–900 cm.$^{-1}$ region as arising from motions of the $NH_2$ group.

Other infra-red spectra of amido- and imido-phosphates have been reported, as follow: monopotassium, monoammonium monoamidophosphates,[525] disilver monoamidophosphate,[525-6] disodium monoamidophosphate,[526, 667] monosodium monoamidophosphate,[525, 667] monobarium monoamidophosphate and barium monoamidophosphate monohydrate, monomagnesium monoamidophosphate and magnesium monoamidophosphate heptahydrate, monoamidophosphoric acid,[667] zinc and thallous monoamidophosphate,[526] zinc diamidophosphate,[526] tetrasodium, dipotassium dihydrogen (and deuterated salt), tetrapotassium, zinc, silver and thallous imidodiphosphates,[526] ($Ag_4P_2O_6NAg$),[526] sodium, sodium dizinc and thallous di-imidotriphosphates, silver and thallous di-imidotrimetaphosphates and thallous di-imidotrimetaphosphate-thallous hydroxide, ($Tl_3P_3O_7(NH)_2.TlOH$).[526]

The crystal structure of potassium amidotriphosphate tetrahydrate, $K_4P_3O_9NH_2, 4H_2O$, has been determined.[1345] The cell is triclinic, with $a = 6{\cdot}08$, $b = 10{\cdot}06$, $c = 12{\cdot}72$ A., $\alpha = 95{\cdot}9°$, $\beta = 91{\cdot}7°$, $\gamma = 107{\cdot}1°$, $Z = 2$, space group $P\bar{1}$. The amidotriphosphate anion is similar to that of triphosphate with one terminal oxygen replaced by an amido group. The anion has a less extended configuration than the anion of sodium triphosphate. The structure consists of layers of amidotriphosphate anions and potassium atoms alternating with layers of water molecules.

The phosphorus nuclear magnetic resonance spectrum of the amidotriphosphate ion, $(PO_3.O.PO_2.O.PO_2NH_2)^{4-}$, has been reported.[663] The amidophosphate end group has a chemical shift of +0·2 p.p.m., and the spin-spin splitting between the amidophosphate end group and the middle group is 18 c/s. The phosphorus nuclear magnetic resonance spectra of monosodium monoamidophosphate and of diamidophosphoric acid have been determined.[171] The chemical shifts are −3 and +3·5 p.p.m. respectively, the latter figure being regarded[171] as doubtful.

NMR data for a series of amido and imido phosphates have been reported[1346-7] and are tabulated below. The substitution of –NH– for –O– in chain and ring compounds generally results in negative displacement of the phosphorus shift.[1346]

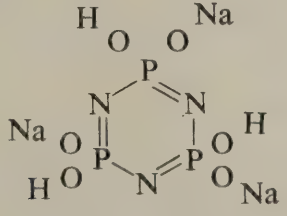
| Compound | $^{31}P$ chemical shift (ref. $H_3PO_4$) p.p.m. | Reference |
|---|---|---|
| $HPO_2(NH_2)_2$ | +0·2 | 1347 |
| $Na_2PO_3NH_2$ | −8·9 | 1348 |
| $NaPO_2(NH_2)_2$ | −14·5 | 1347–8 |
| $NaPOS(NH_2)_2$ | −54·2 | 1347–8 |
| $Na_4O_3PNHPO_3$ | −2·7 | 1347–8 |
| $Na_5O_3PNHPO_2NHPO_3$ | −1·6 | 1347–8 |

The infra-red spectra of some (tetraphenyl phosphonium) diazophosphoromonothioates, $PSO(N_3)_2^-$, and azophosphorothiofluoridates, $PSON_3F^-$, have been reported[1348] and some assignments made, including the following: $PSO(N_3)_2^-$, $\nu_{as}N_3$ 2125/2155, $\nu_sN_3$ 1270/1290, $\nu$PO 1215/1230, $\nu$PS 610 cm.$^{-1}$; $PSON_3F^-$, $\nu_{as}N_3$ 2150, $\nu_sN_3$ 1272, $\nu$PO 1210/1230, $\nu$PF 798, $\nu$PS 630.

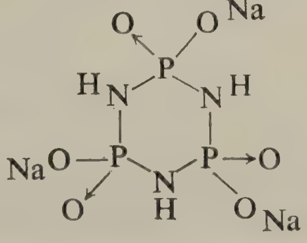
### TRIMETAPHOSPHIMATES

The acids and salts obtained from the hydrolysis of phosphonitrilic chlorides have been described as phosphonitrilates (I) and as trimetaphosphimates (II), depending on the situation of the hydrogen atoms.

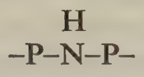
I



II



The first report[656] of the infra-red spectra of this class of compounds described them as of type I, on the basis of the assignment of P–O–H bands at 2700 cm.$^{-1}$ and 1400–1220 cm.$^{-1}$, and P=N bands at 1200–900 cm.$^{-1}$ Later work[526] using anhydrous samples and mulling techniques, showed that the bands around 2700 cm.$^{-1}$ were absent. The bands in the 1400–1200 cm.$^{-1}$ region were related to the



$$-P-\overset{H}{N}-P-$$

grouping, and those in the 1200–900 cm.$^{-1}$ region to P(O)–O$^-$ rather than to P=N. The Raman spectrum of sodium trimetaphosphimate[598] shows strong similarities to that of sodium trimetaphosphate, providing further support for the trimetaphosphimate structure. It appears from this evidence that the salts are most likely to be in the trimetaphosphimate form (II), and this conclusion is supported by chemical evidence (see page 221). Detailed assignments of the infra-red spectra of the normal and deuterated tetrametaphosphimic acids, both anhydrous and dihydrated, have been proposed on this basis.[921–2] Stretching vibrations of the $PO_2H$ groups were assigned in the regions 793$^{-}$945 cm.$^{-1}$ (symmetrical) and 1068–1207 cm.$^{-1}$ (antisymmetrical). Ring stretching vibrations were assigned at 524–624 cm.$^{-1}$ (breathing) and 840–1040 cm.$^{-1}$ (antisymmetrical). NH and ND bending vibrations were assigned at 758–813 and 583–611 cm.$^{-1}$ respectively. The salts of which the infra-red spectra have been reported are the trimetaphosphimates of sodium magnesium (hexahydrate), sodium calcium (tetrahydrate), sodium strontium (tetrahydrate) and sodium barium ($NaBa(PO_2NH)_3,1{\cdot}5H_2O$), the tetrametaphosphimates of dipotassium dihydrogen, dirubidium dihydrogen, sodium (2·5-hydrate), calcium (tetrahydrate), barium (dihydrate), copper (-ic, tetrahydrate), nickel (2·5-hydrate) and lead (hydrate),[656] trimetaphosphimic acid,[526] the trimetaphosphimates of sodium dihydrogen (dihydrate), potassium (and deuterated salt), thallium (ous) and thallium-thallous hydroxide [$Tl_3(PO_2NH)_3.TlOH$], the tetrametaphosphimates of ammonium (tetrahydrate), disodium dihydrogen, sodium (trihydrate), potassium and thallium (ous),[526] the trimetaphosphimates of sodium (tetrahydrate) and silver, and the tetrametaphosphimates of diammonium dihydrogen and silver.[525–6]

The infra-red and Raman spectra of potassium trimetaphosphimate, $K_3(PO_2NH)_3$, and its deuterated analogue have recently been determined,[1351] both in the crystal and in solution. It was concluded that the anion had $C_{3v}$ symmetry both in the crystal and in solution. Assignment (for the solution) included the following: $\nu_{as}PO_2$ 1207($A_1$), 1170($E$); $\nu_sPO_2$ 1107($A_1$), 1053($E$); $\nu$P–NH–P 953, 830($E$); $\nu_s$P–NH–P 755($A_1$). Assignments in the crystal were similar.

The phosphorus nuclear magnetic resonance spectrum of sodium trimetaphosphimate has been determined.[171] There is a single peak at a chemical shift of +1 p.p.m., confirming the ring structure. The shift for potassium tetrametaphosphimate has been reported[1347] as +3·7 p.p.m. $^{31}$P NMR data for sodium mon-, di and tri-imidotrimetaphosphate have been reported[1346] as follows: mono +10·4($\alpha$), +20·2($\beta$) p.p.m.; di +4·2($\alpha$), +7·9($\beta$) p.p.m., $J\alpha\beta=7$ c/s; tri(trimetaphosphate) +1·5 p.p.m.

Preliminary *X*-ray structure data have been reported for tetrametaphosphimic acid and some of its salts.[666] Dipotassium dihydrogen tetrametaphosphimate is orthorhombic, with $a=13{\cdot}89$, $b=8{\cdot}07$, $c=5{\cdot}03$ A. and a bimolecular cell. The corresponding rubidium salt is also orthorhombic with a bimolecular cell, of dimensions $a=14{\cdot}03$, $b=8{\cdot}34$, $c=5{\cdot}06$ A., and is isomorphous with the potassium salt. The diammonium salt is reported to be isomorphous with the other salts, with $c=5{\cdot}08$ A. The phosphimate formulation for these compounds has been confirmed by crystal structure determinations on two of the salts.[1349–50] Sodium trimetaphosphimate tetrahydrate,[1349], $Na_3(NHPO_2)_3,4H_2O$, is monoclinic with $a=16{\cdot}976$, $b=7{\cdot}834$, $c=8{\cdot}918$, $\beta=97°\ 08'$, $Z=4$, space group $P2_1/n$. The ring has a chair configuration with approximate skeletal symmetry $C_{3v}$. The three-dimensional difference map clearly shows the hydrogens linked to the nitrogens of the $(N–P)_3$ ring. The hydrogen locations have a lower symmetry than the skeletal, reducing the approximate molecular symmetry from $C_{3v}$ to $C_s$. Average bond lengths are P–N 1·68 A., P–O 1·495 A., with angles PNP 123°, NPN 104·5°, OPO 118°. Tetrametaphosphimic acid dihydrate,[666, 1350] $H_4(NHPO_2)_4,2H_2O$, is orthorhombic, with $a = 13{\cdot}98$, $b = 8{\cdot}32$, $c = 5{\cdot}04$ A., $Z = 2$, space group $P2_12_12_1$. The anion has a tub configuration of approximate symmetry $S_4$. The positions of the hydrogens were not determined directly but their location on the nitrogens was deduced from other structural evidence. The anions are linked by short O···H···O bonds into two-dimensional sheets perpendicular to the *c* axis. These sheets are connected into a three-dimensional net by N–H···O bonds. The PN bonds are all equal within experimental error, at 1·66 A. There are two types of PO bond: PO–H··· forming part of the network linkage (PO = 1·52 A.) and PO bonds not directly linked to hydrogen ($1{\cdot}48_5$ A.).

### Un-ionized Phosphorus–Nitrogen Compounds

The Raman and infra-red spectra of phosphoryl triamide, $OP(NH_2)_3$, and the infra-red spectrum of thiophosphoryl triamide, $SP(NH_2)_3$, have been determined.[667] The spectra were assigned on the basis of $C_{3v}$ symmetry. The symmetrical P–N stretching vibration is assigned at 832 cm.$^{-1}$ in the Raman (aqueous solution), but is apparently lowered to 725 cm.$^{-1}$ in the infra-red (KBr disc) probably as a result of hydrogen bonding. The corresponding band in $SP(NH_2)_3$ is assigned at 715 cm.$^{-1}$ in the infra-red. The PO and PS vibrations are assigned at 1174–1200 and 860 cm.$^{-1}$ respectively. The $^{31}$P NMR chemical shift of phosphoryl triamide is[1347–8] $-22{\cdot}0$ p.p.m. relative to 85% $H_3PO_4$.

The thermal dehydration of phosphoryl triamide to a compound of approximate empirical composition PNO has been followed[1352, 1390] by infra-red spectroscopy. The dehydration of deuterated products was also examined. Evidently reaction with atmospheric water leads to breaking of the PN bonds, the substitution of OH for $NH_2$, then a tautomeric rearrangement to give P–O–P bonds. Spectra were presented for different N:P ratios from 3 down to 0·81. The final product showed infra-red evidence for a structure consisting mainly of P–O–P and P–N–P linkages.[1352]

Later[1353] work on the infra-red spectrum of thiophosphoryl triamide proposes different assignments from those above; the 715 cm.$^{-1}$ band is assigned to the symmetric, rather than the asymmetric, PN stretch, and the PS stretching vibration is assigned at 615 cm.$^{-1}$ Some assignments were also proposed[1353] for the related compound $SP(NH–NH_2)_3$, including PNN stretching vibrations at 813, 865, 909 and 957 cm.$^{-1}$

The $^{31}$P NMR shift of thiophosphoryl triamide has been reported as $-61{\cdot}1$ p.p.m. in aqueous solution[1347–8] and $-59{\cdot}4$ p.p.m. in dimethylformamide solution,[1354] both relative to 85% $H_3PO_4$.

The crystal structure of triamidophosphorusborane, $(H_2N)_3PBH_3$, has been determined.[715] The unit cell is monoclinic, with $a = 9{\cdot}414$, $b = 9{\cdot}492$, $c = 6{\cdot}227$ A., $\beta = 100{\cdot}3°$, $Z = 4$. The bonding around the phosphorus atom is not quite tetrahedral, but the P–N bonds are all equal and the distortions of the angles from a tetrahedral arrangement are in the directions expected from a consideration of the intermolecular contacts. The $NH_2$ groups are therefore regarded as chemically equivalent, the distortions being due to crystal packing. Bond lengths are P–N = 1·653, P–B = 1·887 and angles N–P–N 99·6–116·8°, N–P–B 123·3–109·0°.

The infra-red spectrum of phosphorus tricyanide has been reported.[764] Only two bands were observed, at 2195 and 642 cm.$^{-1}$ in the vapour, which were assigned to C≡N and P–C stretching vibrations respectively.

### Phosphonitrilic Compounds

The bonding in phosphonitrilic compounds is considered to be analogous to that in aromatic compounds, with $\pi$-bonding between the *p*-orbitals of the nitrogen atoms and the *d*-orbitals of the phosphorus atoms.[676] Such $\pi$-bonding leads to equality and shortness of the ring bonds, and many of the other structural and spectroscopic data described below have also been related to the system of $\pi$-bonding. The nature of the $\pi$-bond system has been considered in detail.[676-8,689,923]

## PHOSPHONITRILIC CHLORIDES

The crystal structure of triphosphonitrilic chloride, $(PNCl_2)_3$, has been determined.[669,672-4,679,924-5] The structure[674] is orthorhombic, with $a = 14{\cdot}15$, $b = 12{\cdot}99$, $c = 6{\cdot}19$ A., $Z = 4$, space group *Pnma*. The $(PNCl_2)_3$ molecules lie on mirror planes which are perpendicular to the six-membered $P_3N_3$ ring. The results of References 674 and 925, although in general agreement, differ in detail. In Reference 674 slight deviations of the ring from planarity are regarded as due to crystal forces; slight differences in the ring bond lengths are regarded as insignificant. In Reference 925, on the other hand, the ring bond lengths appear to be significantly different, and all the P and N atoms appear to be equidistant from, and on opposite sides of, the mean plane, giving a chair-shaped ring. However, the treatment of the standard deviations in Reference 925 is incorrect[926] giving misleadingly low values, and the results may also be criticized[926] for the use of common isotropic temperature factors when very strong anisotropic thermal vibrations are present. For these reasons the results of Reference 674 are to be preferred, although there is an error[926] in the calculation of the mean plane. A mean structure has been calculated[926] weighted 2:1 in favour of Reference 674. This gives more regular results for the bond lengths and angles than either of the independent determinations, with a very small deviation of the ring from planarity. The bond lengths are: P–N, 1·59, 1·58, 1·58 A.; P–Cl, 1·97, 1·97, 1·98, 1·98 A. Angles are: N–P–N, 118·5, 119·5°; P–N–P, 120·7, 120·5°; Cl–P–Cl, 102·1, 101·8°, with the Cl–P–Cl planes effectively perpendicular to the plane of the ring. The triphosphonitrilic chloride molecule therefore approximates to $D_{3h}$ point symmetry; earlier electron diffraction results are in agreement with this.[670]

The structure of the metastable[675] form of tetraphosphonitrilic chloride, $(PNCl_2)_4$, has been determined[671] and recently refined.[927] The tetragonal two-molecule cell has $a = 10{\cdot}844$, $c = 5{\cdot}961$ A.,[927] space group $P4_2/n$. Molecules of $(PNCl_2)_4$ with boat-shaped rings of $P_4N_4$ lie on $\bar{4}$ axes. The point-group symmetry of the molecule is $S_4$. The bond lengths[927] are: $P–N = 1{\cdot}57_0$ and $1{\cdot}56_9$ A., $P–Cl = 1{\cdot}985$ and $1{\cdot}993$ A.; angles are: $N–P–N = 121{\cdot}2°$, $P–N–P = 131{\cdot}3°$, $Cl–P–Cl = 102{\cdot}8°$. The other form[675] is also tetragonal, with space group $P4_2/n$, and cell dimensions $a = 10{\cdot}82 \times \sqrt{2}$, $c = 5{\cdot}95$ A.; space group and packing considerations lead to the conclusion that the molecules must be on sites of $C_i$ symmetry,[680] although the results of an infra-red study are in conflict with this.[681] A preliminary note[1362] on a crystal structure determination confirms the $C_i$ site symmetry. Bond length and angle data were quoted as follows: PN 1·56, PCl 1·99 A., NPN 122°, PNP 135°, ClPCl 103°.

Pentameric phosphonitrilic chloride, $(PNCl_2)_5$, is orthorhombic, space group $P2_12_12_1$, with $a = 15{\cdot}48$, $b = 19{\cdot}44$, $c = 6{\cdot}26$ A., $Z = 4$.[682,1355] The ten atoms in the phosphonitrilic ring are surprisingly close to a planar configuration. The average PN bond length is 1·52 A., individual bonds varying between 1·49 and 1·52 A. in a non-systematic way. The average ring angles are NPN 118·4°, PNP 148°, with a range of 134°–159°. Of two or three forms of hexameric phosphonitrilic chloride, $(PNCl_2)_6$, the cell dimensions of a triclinic form are $a = 10{\cdot}6$, $b = 10{\cdot}7$, $c = 11{\cdot}4$ A., $\alpha = 93{\cdot}5°$, $\beta = 90°$, $\gamma = 117°$, $Z = 2$. Octameric phosphonitrilic chloride, $(PNCl_2)_8$, is monoclinic, with $a = 24{\cdot}7$, $b = 6{\cdot}2$, $c = 20{\cdot}4$ A., $\beta = 111°$, $Z = 4$, space group $C2/c$ or $Cc$.[913]

The *X*-ray fibre pattern of the stretched phosphonitrilic chloride high polymer has been investigated.[714] A helical chain configuration was suggested,[714,928] and the dimensions of an orthorhombic cell reported as $a = 11{\cdot}07$, $b = 4{\cdot}92$, $c = 12{\cdot}72$ A. In a more recent paper[929] it is suggested that the best agreement with the observed *X*-ray pattern is obtained from a double helical configuration with $P–N = 1{\cdot}60$ A., and angles $N–P–N = 119°$, $P–N–P = 127°$. This is quite close to a planar PN skeleton.

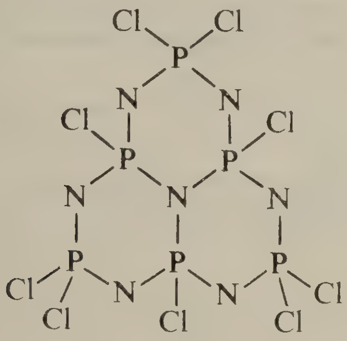
The infra-red[215, 681, 684, 686, 1356–7, 1359–60, 1363–4] and Raman[681, 683, 684, 1356–7, 1360] spectra of trimeric phosphonitrilic chloride have been extensively investigated.[681, 683–4, 1356–7, 1359–60, 1363–4] The spectra confirm that the symmetry of the molecule is $D_{3h}$ in solution[681, 684] and in the vapour.[681] The first assignments[684] of the spectra have been considerably revised,[681, 1356–7, 1359–60, 1363–4] and have been the subject of considerable controversy. Polarized infra-red measurements with oriented samples, including mixed crystals with triphosphonitrilic bromide,[1359] have been employed[1359, 1364] in attempts to sort out the assignments. The most prominent feature of the infra-red spectrum is a very strong band, arising from a degenerate member of a series[681, 687] of stretching vibrations of the phosphonitrilic ring, at 1218 cm.$^{-1}$ Some force constants calculated from the $A_1'$ frequencies,[685] were based on incorrect assignments. Later force constant work,[1365] though more complete, was based on assignments which also proved to be controversial.

In tetraphosphonitrilic chloride, $(PNCl_2)_4$, the characteristic ring absorption in the infra-red moves to 1310 cm.$^{-1}$.[681, 684] The infra-red and Raman spectra[681, 684, 1356, 1359, 1371] were first interpreted[684] as supporting $D_{4h}$ symmetry for the molecule, indicating a planar ring, although $D_{2d}$ symmetry was not excluded. Other work[681] suggested that the ring is not planar in the vapour; later work[1356] supported a planar configuration, while the latest work[1371] again supports $D_{2d}$ symmetry in solution. It is clear, however, from the difference in symmetry in the two forms that the molecule is flexible.

The ring absorption in pentaphosphonitrilic chloride, $(PNCl_2)_5$,[681, 686, 930] is split into a doublet, with components at 1285 and 1345 cm.$^{-1}$ in the vapour[681] owing to a resolution of the ring degeneracy. This indicates a low symmetry which is also indicated by the number of polarized bands in the Raman spectrum and by other data.[681]

The infra-red spectra of the higher cyclic phosphonitrilic chlorides up to the hexamer, $(PNCl_2)_6$,[686, 930] heptamer[686, 931] and octamer,[931] have been determined. The characteristic ring absorption moves to lower frequencies with increasing ring size, lying at 1325, 1310 and 1305 cm.$^{-1}$, in the hexamer, heptamer and octamer respectively. An oily mixture of cyclic phosphonitrilic chloride molecules of average composition $(PNCl_2)_{12-13}$ absorbs at 1257 cm.$^{-1}$.[931] The corresponding band in the rubbery $(PNCl_2)_n$ high polymer occurs at 1215 cm.$^{-1}$ [931]

The infra-red spectrum of the phosphonitrilic chloride, $P_6N_7Cl_9$, which is thought[682] to have the following polycyclic structure:

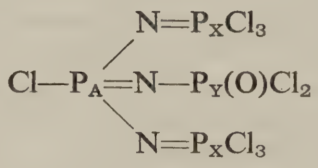


has been reported.[686] The characteristic phosphonitrilic absorption occurs at 1285 cm.$^{-1}$

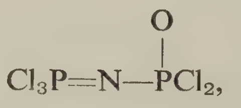
The ultra-violet spectra of phosphonitrilic chloride polymers up to octamer, and the nitrilohexamer, have been reported.[675, 682, 686, 1366–7] They give no structural information. The trimer and tetramer both show peaks[1366] at 200 and 210 mμ. The spectra of $(PNCl_2)_3$–iodine–heptane solutions have been studied.[1367]

The phosphorus nuclear magnetic resonance spectra of the phosphonitrilic chloride polymers up to the octamer have been determined.[171, 675, 688, 1375] A single phosphorus peak is observed in all cases, confirming the cyclic nature of the molecules. The chemical shifts (relative to 85% orthophosphoric acid) are −19·7 p.p.m. for the trimer, +7·4 p.p.m. for the tetramer, and approximately +18 p.p.m. for the other compounds.[675, 688, 1375] It has been suggested[923] that the changes in chemical shift with increasing ring size may be due to increasing delocalization of the nitrogen lone-pair electrons.

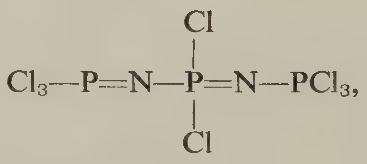
The nuclear magnetic resonance spectra of several non-cyclic chlorine-containing phosphonitrilic compounds have been described[675, 932–6, 1368–9] and used to determine their structures.[932–6, 1368–9] The compound $P_2NOCl_5$ [932–3, 936] has been shown to have the structure $Cl_3P_A{=}N{-}P_B(O)Cl_2$. The chemical shifts of $P_A$ and $P_B$ are +0·1 p.p.m. and 14·2 p.p.m. respectively (referred to 85% orthophosphoric acid), and the coupling constant $J_{AB}$ is 15·4 c/s.[932] The infra-red spectrum of this compound is also reported[933] and shows the characteristic strong phosphonitrilic absorption at about 1340 $cm.^{-1}$. It is stated, on the basis of the infra-red and nuclear magnetic resonance spectra, that the compound described as $P_4O_4Cl_{10}$ [292, 937–40] is in fact $P_2NOCl_5$ (see page 577). The compound $P_3NCl_{12}$ [934, 936] has the structure $[Cl_3P{=}N{-}PCl_3]^+PCl_6^-$. The chemical shifts (in nitromethane solution), relative to 85% orthophosphoric acid, are about 305 p.p.m. for the $PCl_6^-$ ion and −21·4 p.p.m. for the $[P_2NCl_6]^-$ ion. The analogous compound with an extra phosphorus atom[934, 936] is $P_4N_2Cl_{14}$, with the structure $[Cl_3P_B{=}N{-}P_ACl_2{=}N{-}P_BCl_3]^+PCl_6^-$. The chemical shifts are respectively −12·5, 13·6 and approximately 305 p.p.m. for $P_B$, $P_A$ and $PCl_6^-$. The coupling constant $J_{AB}$ is 45·3 c/s. The members of the series of compounds $[Cl_3P{=}N(PNCl_2)_nPCl_3]^+PCl_6^-$ give peaks in almost identical positions.[935] The compound $P_3N_2OCl_7$ has the structure $Cl_3P_B{=}N{-}P_ACl_2{=}N{-}P_B(O)Cl_2$.[934, 936] The chemical shifts are respectively −7·1, +20 and +13·4 p.p.m. for $P_X$, $P_A$ and $P_B$. The coupling constants $J_{AX}$ and $J_{AB}$ are 29·5 and 26·7 c/s respectively; $J_{BX}$ was too small to be detected. The structure of the compound $P_4N_3OCl_9$[934] has been shown to be:


N=P<sub>X</sub>Cl<sub>3</sub>
Cl—P<sub>A</sub>=N—P<sub>Y</sub>(O)Cl<sub>2</sub>
N=P<sub>X</sub>Cl<sub>3</sub>

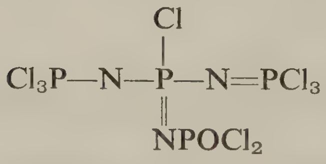
Chemical shifts are 29·6, 1·9 and 13·6 p.p.m. for $P_A$, $P_X$ and $P_Y$ respectively. The coupling constants $J_{AX}$ and $J_{AY}$ are 28·7 c/s and 31·0 c/s respectively; $J_{XY}$ was too small to be detected. The compounds $P_2NOCl_5$, $P_2NCl_2$ and $P_4N_3OCl_9$ were stated[1369] to have the following structures, determined by NMR, although no data were reported:



$$\mathrm{Cl_3P{=}N{-}\overset{\displaystyle O}{\overset{|}{P}}Cl_2},$$



$$\mathrm{Cl_3{-}P{=}N{-}\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{P}}}}{=}N{-}PCl_3},$$



$$\mathrm{Cl_3P{-}N{-}\underset{\displaystyle NPOCl_2}{\underset{\|}{\overset{\displaystyle Cl}{\overset{|}{P}}}}{-}N{=}PCl_3}$$

The compound $NP_2Cl_7$,[1368, 1370] indicated by infra-red spectra[1368] to be $NPCl_2,PCl_5$, was found by NMR[1368] to ionize in nitrobenzene solution to $PCl_4^+NPCl_3^-$.

Chlorine nuclear quadrupole resonance spectra have been reported for several phosphonitrilic chlorides.[690–4, 1373–4] For the trimer four lines are found at about 28 Mc/s[690–4] with an overall spacing of about 0·3 Mc/s at both 15°C. and −195°C.[694, 1373] Two of the lines have twice the intensity of the other two, and this observation is in complete agreement with the crystal structure,[674] since the $(PNCl_2)_3$ molecules lie on mirror planes. For the tetramer of known crystal structure,[671] metastable form, there are only two non-equivalent chlorine atoms, and only two peaks are therefore expected in the nuclear quadrupole resonance spectrum. The observed spectrum[694, 1373-4] is in agreement, showing two peaks at about 28 Mc/s with a separation which increases with temperature. An earlier report[692] agrees with this, but other reports,[690-1, 693] describe four lines. These results may refer to the form of different crystal structure,[675] for which four lines of equal intensity are expected,[680-1] but one report[691, 695] states that the lines are of unequal and variable intensity. The latest work[1373-4] on this form of the tetrameric chloride does report four lines, in agreement with the crystal structure, although in one report[1373] the lines are stated to be of unequal intensities (2:3:2:3), which is inconsistent with four molecules per unit cell. The other report[1374] does not mention any unequal intensities but notes that the separation between the two inner frequencies appears to extrapolate to zero at the melting point, suggesting a transition to $C_{2h}$ symmetry in the melt.

Nine weak lines have been observed in the pentamer chloride at −195°C., and one of two phases of the hexamer chloride showed 12 lines at −195°C.[694]

### PHOSPHONITRILIC FLUORIDES

The crystal structure of triphosphonitrilic fluoride, $(PNF_2)_3$, has been investigated[696-8] and accurately determined.[698] The cell is orthorhombic, with $a = 6{\cdot}948$, $b = 12{\cdot}190$, $c = 8{\cdot}723$ A., $Z = 4$, with space group *Pnma.*[698] The cyclic molecules lie on a mirror plane which is perpendicular to the ring, and have point symmetry approximating to $D_{3h}$. The P–N bond lengths are 1·546, 1·563 and 1·572 A. The average P–F bond length is 1·521 A.; the ring angles are 119·6° and 121·1° at the nitrogen and 119·5° and 119·3° at the phosphorus. The space group and the type of packing are the same as in triphosphonitrilic chloride.

The crystal structure of tetraphosphonitrilic fluoride, $(PNF_2)_4$, has been investigated[696-7, 699-700] and accurately determined.[699-700] The structure is monoclinic, with $a = 7{\cdot}40$, $b = 13{\cdot}83$, $c = 5{\cdot}16$ A., $\beta = 109{\cdot}5°$, space group $P2_1/a$, $Z = 2$. The molecule is centrosymmetric and approximates closely to $D_{4h}$ point symmetry, with a planar ring. The deviations from $D_{4h}$ symmetry, the main one of which is a displacement of the fluorine atoms so that they are not mirrored by the plane of the ring, are due to crystal forces. The deviations of the nitrogen atoms from the plane of the phosphorus atoms are not significant. The non-bonded separations between atoms in adjacent molecules are very large, suggesting that the fluorine atoms may be charged. The P–N bond length, 1·51 A., is much shorter, and the P–N–P angle 147·2° much larger, than the corresponding values in $(PNCl_2)_4$. The P–F bond length is 1·51 A.; other angles are N–P–N = 122·7°, F–P–F = 99·9°, N–P–F = 108·0°. Another form of $(PNF_2)_4$, obtained at low temperatures, has the same space group, $P2_1/a$, and the same cell dimensions except that *c* is doubled. Force constants have been calculated,[1365] but some of the assignments used[681] have been questioned in later work.[1356]

The infra-red[681, 687, 701-2, 1356, 1358] and Raman[681, 687, 702, 1358] spectra of triphosphonitrilic fluoride show[681, 702, 1358] that the molecule has $D_{3h}$ symmetry with a planar six-membered ring like the corresponding chloride. The characteristic phosphonitrilic ring absorption in the infra-red occurs at 1297 $cm.^{-1}$. Another strong absorption at 973 $cm.^{-1}$ was attributed[702, 1358] to another ring vibration, but has since been shown[681] to arise from the unsymmetrical in-phase $PF_2$ stretching vibration.

In the infra-red spectrum[681, 687, 701-2] of tetraphosphonitrilic fluoride, the characteristic phosphonitrilic absorption is split, with components at 1419 and 1438 $cm.^{-1}$, indicating resolution of the degeneracy, and the infra-red and Raman[681, 687, 702] spectra have been interpreted[702] as indicating $C_{2h}$ molecular symmetry. Other work, however,[681] has shown (from the variability of the spectra between different phases, and the contrast between the high symmetry in the crystal[700] and the low symmetry in other phases) that the molecule is very flexible. It has been claimed[1356] that the spectra indicate $D_{4h}$ symmetry; the splitting of the phosphonitrilic absorption was attributed to a Fermi doublet.

The numbers of polarized Raman bands, infra-red bands and Raman/infra-red coincidences in the spectra of pentaphosphonitrilic fluoride indicate that the symmetry is low.[681] The variability of the spectra again shows that the molecule is flexible. The characteristic phosphonitrilic absorption occurs at 1439 cm.$^{-1}$

The infra-red spectra of higher polymers of phosphonitrilic fluoride up to $(PNF_2)_{17}$ and of the rubbery high polymer, have been determined.[687] Regularities in an extensive system of infra-red bands arising from symmetrical $PF_2$ stretching vibrations show that all the molecules are monocyclic.[687] As in the chlorides, the characteristic phosphonitrilic infra-red absorption decreases in frequency with increasing ring size once the pentamer is reached. The frequencies, in order of ascending ring size from the hexamer to the undecamer, are 1408, 1400, 1386, 1375, 1363 and 1357 cm.$^{-1}$.[687]

The mass spectra of trimeric and tetrameric phosphonitrilic fluoride have been reported[703] to be in agreement with the cyclic structure.

The phosphorus and fluorine nuclear magnetic resonance spectra of the phosphonitrilic fluorides up to the decamer, with the exception of the hexamer, have been determined.[688] The phosphorus chemical shifts, relative to 85% orthophosphoric acid, are respectively $-9$, $+18$, $+23$, $+23{\cdot}5$ and $+24$ p.p.m. for the trimer, tetramer, pentamer, heptamer and octamer to decamer respectively. The fluorine shifts, relative to trifluoroacetic acid, are respectively $+115{\cdot}5$, $+114$, $+109{\cdot}3$, $+108{\cdot}5$, $+108{\cdot}2$, $+108{\cdot}2$, $+108{\cdot}5$ p.p.m. in trimer, tetramer, pentamer, heptamer, octamer, nonamer and decamer respectively. Both spectra are split by spin-spin interaction between the phosphorus and fluorine nuclei, the fluorine spectrum into a doublet by the single phosphorus of the $PF_2$ group, the phosphorus spectrum into a 1–2–1 triplet by the two fluorine nuclei of the $PF_2$ group. The spin-spin coupling is about 900 c/s. Both fluorine and phosphorus spectra show further fine structure, presumably due to interaction between phosphorus and remote fluorines. This structure, which is of the order of 50 c/s wide, is most clearly defined in the spectra of the trimer, and becomes less resolvable as the ring size increases.

The infra-red[681, 704] nuclear magnetic resonance[704] and Raman[706] spectra of several trimeric phosphonitrilic fluoride-chlorides have been determined, and the infra-red and nuclear magnetic resonance spectra used[704] to show that the compounds are the triphosphonitrilic, 1,1-difluoride 3,3,5,5-tetrachloride, 1,1,3-trifluoride, 3,5,5-trichloride and 1,1,3,3-tetrafluoride 5,5-dichloride. The characteristic phosphonitrilic infra-red absorptions lie between those of triphosphonitrilic chloride and triphosphonitrilic fluoride, at 1246 and 1226, 1258 and 1237, 1277 and 1253 cm.$^{-1}$ respectively.[704] The nuclear magnetic resonance spectra of the 1,1-difluoride 3,3,5,5-tetrachloride have been analysed in detail,[705] and the spin-spin coupling constants obtained. The results are $J_{PF}$ (directly connected) $= +934$ c/s $J_{PF}$ (nonbonded) $= -14$ c/s, $J_{PP'} = -100$ c/s. The NMR spectra of triphosphonitrilic monofluoride pentachloride have also been studied.[1372] The $^{31}P$ spectrum shows an $AB_2$ system with $\delta_A = -14{\cdot}4$ p.p.m., $\delta_B = -23{\cdot}0$ p.p.m. (ref. $H_3PO_4$), $J_{AF} = +1012$ c/s, $J_{BF} = -11$ c/s, $J_{AB} = -78{\cdot}3$ c/s.

Spectroscopic data have also been reported[1376] for the complete series of tetrameric phosphonitrilic fluoride chlorides and the geminal substitution pattern confirmed by $^{31}P$ and $^{19}F$ NMR. The phosphonitrilic infra-red absorption frequencies are as follows, in order of increasing fluorine substitution: 1330 (1F), 1346 (2F), 1362 (3F), 1377 (4F), 1390 (5F), 1400 (6F), 1408 (7F). $^{19}F$ NMR data (shifts relative to $P_3N_3F_6$) were as follows: $P_4N_4FCl_7$ $\delta = -30$ p.p.m., $J_{PF} = 950$ c/s; $P_4N_4F_2Cl_6$ $\delta = 0{\cdot}9$, $J = 925$; $P_4N_4F_3Cl_5$ $\delta = 0{\cdot}3$, $J = 925$ ($PF_2$) $\delta = -32{\cdot}5$, $J = 950$ (PFCl); $P_4N_4F_4Cl_4$ $\delta = 0{\cdot}3$, $J = 900$; $P_4N_4F_5Cl_4$ $\delta = 0{\cdot}0$, $J = 900$ ($PF_2$), $\delta = -32{\cdot}5$, $J = 975$ (PFCl); $P_4N_4F_6Cl_4$ $\delta = -1{\cdot}4$, $J = 880$ (intensity 4) and $\delta = 0{\cdot}5$, $J = 900$ (intensity 2); $P_4N_4F_7Cl$ $\delta = 0{\cdot}8$, $J = 900$ ($PF_2$), $\delta = -33{\cdot}5$, $J = 925$ (PFCl); $P_4N_4F_8$ $\delta = 0{\cdot}4$ p.p.m., $J = 850$ c/s.

## PHOSPHONITRILIC BROMIDES

Triphosphonitrilic bromide[707–9,1377] is isotypic with triphosphonitrilic chloride. The orthorhombic four-molecule cell has $a = 14{\cdot}43$, $b = 13{\cdot}36$, $c = 6{\cdot}63$ A., space group *Pnma*. A two-dimensional refinement of the structure was carried out[1377] and bond length and angle data obtained as follows: PN 1·51, 1·53, 1·54 A. (av. 1·53 A.), PBr 2·08, 2·14, 2·20, 2·22 A., NPN = 116–117°, PNP = 122, 126°, BrPBr = 102–3°. Tetraphosphonitrilic bromide is tetragonal, with $a = 11{\cdot}18$, $c = 5{\cdot}95$ A., $Z = 2$, space group $P4_2/n$.[707]

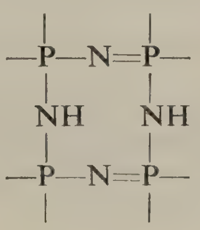
The infra-red[710,1356,1358–9,1371] and Raman[1356,1371] spectra of triphosphonitrilic bromide have been determined. They are very similar to those of triphosphonitrilic chloride. It was concluded[1356,1371] from the spectra that the molecule has $D_{3h}$ symmetry in solution, with a slight deviation to $C_{3v}$ in the crystal.[1371] Polarized infra-red measurements on oriented samples including mixed crystals with the chloride have been made.[1359] The characteristic phosphonitrilic frequency occurs[710–11] at 1178 cm.$^{-1}$ in triphosphonitrilic bromide and 1277 cm.$^{-1}$ in tetraphosphonitrilic bromide.[711] From infra-red[1356,1359,1371] and Raman[1356,1371] spectra this molecule has been described as having $D_{4h}$ symmetry by some workers[1356] and $D_{2d}$ symmetry by others.[1371]

Unit cell data have been reported[712] for three triphosphonitrilic chloride bromides, the pentachloride bromide, the tetrachloride dibromide and dichloride tetrabromide. All are orthorhombic, with four molecules per cell, and cell dimensions as follow: triphosphonitrilic pentachloride bromide, $a = 14{\cdot}24$, $b = 13{\cdot}00$, $c = 6{\cdot}28$ A.; tetrachloride dibromide, $a = 14{\cdot}27$, $b = 13{\cdot}02$, $c = 6{\cdot}34$ A.; dichloride tetrabromide, $a = 14{\cdot}29$, $b = 13{\cdot}33$, $c = 6{\cdot}48$ A. The space group of the tetrachloride dibromide is $Pn2_1a$ or *Pnma*. Recently the infra-red and Raman (solid) spectra of the complete series of triphosphonitrilic chloride-bromides have been reported,[1360] and assignments proposed[1360] on the basis of geminal substitution. For the monobromide pentachloride the Raman spectrum of the solution has also been reported[1360] and polarized infra-red measurements carried out.[1361] The phosphonitrilic absorptions occur as follows[1360]: $P_3N_3Cl_5Br$ 1209, $P_3N_3Cl_4Br_2$ 1201, $P_3N_3Cl_3Br_3$ 1195, $P_3N_3Cl_3Br_4$ 1190, $P_3N_3ClBr_5$ 1183 cm.$^{-1}$. Some infra-red data have also been reported[1358] for the complete series of triphosphonitrilic fluoride bromides. The phosphonitrilic absorptions lie between 1170 and 1400 cm.$^{-1}$ and are all doublets.

## PHOSPHONITRILIC HEXAHYDRAZIDE AND AMIDES

The phosphonitrilic absorption in the infra-red spectra of triphosphonitrilic hexahydrazide, $P_3N_3(N_2H_3)_6$, occurs[713] at 1218 cm.$^{-1}$ The infra-red spectra of tri- and tetraphosphonitrilic amides have been reported.[761] The characteristic phosphonitrilic absorptions occur at 1175 and 1240 cm.$^{-1}$ respectively, with other strong bands at 925, 1575, 3180 and 3300 cm.$^{-1}$ in the trimeric compound and 915, 1565, 3240 and 3360 cm.$^{-1}$ in the tetrameric compound. The phosphonitrilic absorption in triphosphonitrilic diamide tetrachloride, $P_3N_3Cl_4(NH_2)_2$, is broad and shows structure in the published spectrum[762]; the absorption lies between 1175 and 1220 cm.$^{-1}$. The amido-derivatives are generally regarded[1377] as having non-geminal substitution. However, a recent report[1378] claims that $^{31}$P NMR data indicate that triphosphonitrilic diamide tetrachloride and triphosphonitrilic bis(trichlorophosphazide) tetrachloride are geminally substituted.

The amorphous solid, phospham, of empirical composition, $PN_2H$, which is obtained by pyrolysis of phosphonitrilic amides, has been investigated by infra-red spectroscopy.[761,763] A polymeric structure of the type:



is proposed, and bands at 1300 and 950 cm.$^{-1}$ are assigned to vibrations of the P–N=P and P–NH–P linkages respectively.[763]

## SPECTRA–STRUCTURE CORRELATIONS IN PHOSPHORUS COMPOUNDS

### Infra-red Spectra

Most of the assignments of infra-red bands which might provide useful spectra–structure correlations for analytical purposes have been described under individual compounds or groups of compounds. However, some correlations, particularly those which have been mainly derived from the spectra of large groups of organic phosphorus compounds, may be of sufficiently wide application to justify special mention.

P=O STRETCHING VIBRATIONS

The phosphoryl group produces a strong absorption which occurs most frequently in the range 1300–1250 cm.$^{-1}$.[215, 217, 559, 661–2, 664, 765–72, 775, 782] The position of this band is strongly dependent on the electronegativity of the substituents. With strongly electronegative substituents such as fluorine the frequency is higher, as in phosphoryl fluoride,[215, 217, 275–6] which absorbs at 1395–1404 cm.$^{-1}$, while with less electronegative substituents such as carbon and hydrogen the frequency may be shifted below the range quoted above. The full range has been quoted as 1350–1160 cm.$^{-1}$ [770] or 1160–1400 cm.$^{-1}$.[1379] The dependence of frequency on electronegativity has been put on an almost quantitative basis[773, 1379–80] by relations between the frequency and the sum of the electronegativities or 'shift constants' of the substituents:

$$(\mu) = \frac{39{\cdot}96 - \sum x_i}{3{\cdot}995} \quad [773]$$

$$(\nu) = 950{\cdot}1 + 37{\cdot}5 \sum x \text{ cm.}^{-1} \quad [1379]$$
$$(\nu) = 930 + 40 \sum x \text{ cm.}^{-1} \quad [1380]$$

where the $x_i$ are the electronegativities or shift constants of the substituents. Values of these constants for some common inorganic substituents are given in Table XX. The last relationship is stated to hold within ±12 cm.$^{-1}$ for most of the 900 components considered.[1380]

*Table XX.—Phosphoryl Shift Constants*

| Substituent | Shift constant | Reference |
|---|---|---|
| –O–H | 2·3 | 773 |
| H | 2·1 | 773 |
| F | 4·0 | 773 |
| Cl | 3·0 | 773 |
| Br | 2·8 | 773 |
| $NH_2$ | 1·85 | 1380 |
| $N_3$ | 3·0 | 1380 |

The use of Taft substituent constants, instead of electronegativities, has also been suggested.[774]

These shift relations do not apply quantitatively in cases where the molecule contains OH or NH groups which may form hydrogen bonds with the phosphoryl group.[215, 768–71] In these cases the absorption frequency is lowered by 50–80 cm.$^{-1}$, and the range is quoted[770] as 1225–1140 cm.$^{-1}$.

### THE P(O)OH AND P(S)OH GROUPS

In compounds containing the P(O)OH group the absorption due to OH stretching vibrations is considerably displaced from its normal position by hydrogen bonding,[215, 656, 660, 768–9, 779–80, 782] and appears as a broad weak band in the range 2525–2725 cm.$^{-1}$.

In many compounds containing POH linkages as in some other strongly hydrogen-bonded systems, a characteristic trio of bands at around 2700, 2200 and 1600 cm.$^{-1}$ is seen. This trio and its origin have received a great deal of attention in connection with the theory of strong hydrogen-bonding. The subject has recently been reviewed.[1382]

The PO(H) stretching vibration around 1000 cm.$^{-1}$ has also been related[1381] to the electronegativity of substituent groups and a frequency–electronegativity correlation similar to those above has been proposed[1381]:

$$\nu_{\mathrm{PO(H)}} = 650 + 40 \sum x \text{ cm.}^{-1}$$

### THE P-O-P GROUP

The range (for the asymmetric POP stretching vibration) has been quoted as 901–980 cm.$^{-1}$.[1381]

### P–H STRETCHING VIBRATIONS

These vibrations lead to sharp absorptions of medium intensity[215, 525, 660, 765, 767–8, 770, 772] in the range 2440–2288 cm.$^{-1}$. The range 1150–965 cm.$^{-1}$ has been suggested[770] for P–H bending vibrations.

### P═S STRETCHING VIBRATIONS

These vibrations, although clearly assigned between 695 and 753 cm.$^{-1}$ in the thiophosphoryl halides, are much less well characterized in the infra-red spectra than the corresponding phosphoryl vibrations. The intensity of the absorption is variable and is frequently weak, but ranges of 640–680,[1383] 535–862,[1384] 750–600,[215, 660, 664, 776] 845–740[777, 782–3] and 835–713, 675–568 cm.$^{-1}$ [770] have been proposed by different authors. The frequency does not depend directly on the electronegativity of the substituents.[1384] More detailed correlations were proposed within the total range.[1384]

### P–S–(X) VIBRATIONS

Ranges have been proposed[1384] of 493–548 cm.$^{-1}$ for P–S–(H) vibrations, and 460–500 cm.$^{-1}$ for P–S–(P) vibrations.

### P═Se VIBRATIONS

A range of 473–577 cm.$^{-1}$ has been proposed.[1384]

### P–N STRETCHING VIBRATIONS

A correlation between absorption in the range 750–680 cm.$^{-1}$ and the presence of the P–N linkage has been suggested,[660–2] but molecules containing this linkage frequently show no absorption in this region[782] and the correlation should be interpreted with extreme caution. Other, tentative, assignments have been proposed in the 860–940 cm.$^{-1}$ region.[781] A number of indirect correlations have been proposed[1385] for the identification of P–N groups. A range of 1170–1438 cm.$^{-1}$ has been proposed[1385] for the characteristic absorption in phosphonitrilic and related compounds.

**Refs. p. 1230**

### P–F AND P–Cl STRETCHING VIBRATIONS

These vibrations give strong absorptions in the region 900–720 cm.$^{-1}$.[209–12, 215–8, 260–2, 276, 281, 284, 534, 656, 782] If phosphorus trifluoride and phosphoryl fluoride are excluded, the narrower range 890–805 cm.$^{-1}$ has been suggested.[770, 782] A range of 769–760 cm.$^{-1}$ has been suggested for trivalent phosphorus compounds.[770] P–Cl stretching vibrations normally give strong absorptions in the range 580–540 cm.$^{-1}$.[215, 219–20, 243, 660, 664, 777, 782] The wider range 587–435 cm.$^{-1}$ has also been proposed.[770]

## Nuclear Magnetic Resonance Spectra

Besides the inorganic phosphorus compounds of which the nuclear magnetic resonance spectra have been described individually, phosphorus chemical shifts have been measured for several hundred organophosphorus compounds.[171, 226, 612] The shifts of both trivalent and pentavalent compounds extend over a wide range (approximately 500 and 100 p.p.m. respectively), and different substituents give rise to easily measurable differences in chemical shifts. Useful empirical correlation charts may be drawn up,[171, 786] and in some cases the shift contributions of substituents are roughly additive. Empirical correlations between chemical shifts and a bond parameter related to the number of unbalanced $p$ electrons in the valence shell of the phosphorus atom have been developed.[226, 785] Recently, a LCAO-MO calculation of chemical shifts has been made[1386] and charts produced relating the theoretical shift contributions to substituent electronegativities and bond angles. The results were used to estimate $p^{\pi}$–$d^{\pi}$ bonding. In a second paper[1387] the deviation from additivity of shift contributions was calculated and related to $\pi$ bonding and angular changes in the mixed molecules.

Phosphorus–proton spin-spin coupling constants may range up to 700 c/s when the nuclei are directly bonded together,[171, 225, 612] and in compounds containing thiophosphoryl groups the coupling is about 50 c/s weaker than in the corresponding phosphoryl compound.[612] Phosphorus–proton coupling constants where two bonds separate the nuclei are 10–20 c/s, and are lower in phosphoryl than in thiophosphoryl compounds.[612] When three bonds separate the nuclei, the coupling constants are usually of the order of 10 c/s.[226] A relation has been proposed[1391] between the phosphorus–phosphorus coupling constant in unsymmetrically substituted phosphonitrilic compounds and substituent parameters of the different substituents, which are related to their electronegativities.

### *X*-RAY FLUORESCENCE LINE SHIFTS

The phosphorus $K_{\alpha}$ fluorescent line shift in a number of compounds has recently been studied.[1388] Shifts were related to a standard of disodium phosphate ($2\theta =$ 133·233) taken as zero shift. On this scale, various phosphates and tetrasodium pyrophosphate had zero shift, while other values were: phosphorous acid 0·0006 Å., phosphorus pentasulphide 0·0013 Å., phosphorus heptasulphide and sesquisulphide 0·0016 Å., calcium phosphide ($Ca_3P_2$) 0·00185 Å., and red phosphorus 0·00215 Å.

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### SECTION XXXV

# THE ANALYTICAL CHEMISTRY OF PHOSPHORUS

BY S. GREENFIELD AND M. CLIFT

## QUANTITATIVE ANALYSIS

### Orthophosphates

#### GRAVIMETRIC

PRECIPITATION of ammonium molybdophosphate from nitric acid solution, by the addition of ammonium molybdate and ammonium nitrate, may be used both as a means of separation and possibly of determination of orthophosphate. The composition of the yellow precipitate varies with experimental conditions.[1] The reasons for these differences in composition may be found among the following: adsorption of other ions,[2] co-precipitation of molybdic oxide[3] or 12-molybdophosphoric acid,[4] and base exchange reactions.[2, 5] From *X*-ray studies[8] it has been assigned a theoretical formula of $(NH_4)_3[PMo_{12}O_{40}]$.[6-8] There are numerous methods of precipitation[2-5, 9,10]; some give, it is claimed, precipitates of virtually this formula, either before or after washing. In these cases the ammonium molybdophosphate may be weighed as such, usually after drying at 120°–160°C. (although higher temperatures have been used[3, 11]), or as $P_2O_5,24MoO_3$ after heating to 550°C.[2] Other procedures give different but reproducible compositions.[12-5] The precipitation is retarded by sulphuric,[2] hydrochloric[2] and hydrofluoric[16] acids and their ammonium salts, but not by moderate amounts of perchloric acid or ammonium perchlorate. Selenium, tellurium and both pentavalent and tetravalent vanadium also retard precipitation. Silicon, pentavalent arsenic, pentavalent vanadium and hexavalent tungsten react with ammonium molybdate and/or phosphate to give heteropoly complexes such as molybdosilicate, molybdoarsenate, molybdovanadophosphate and tungstophosphate. Bismuth, titanium and zirconium form insoluble phosphates and if present in appreciable amounts may cause losses[17] in the preliminary operations or lead to contamination of the final precipitate. The effect of some of these retardants and/or contaminants can be minimized by the addition of a 10–20 times greater excess of molybdate reagent than the usual amount (this has been given the minimum value of $3\frac{1}{2}$ times the theoretical quantity[5]). This applies particularly in the presence of chloride, sulphate and fluoride ions, although fluoride is best converted to the non-interfering fluoborate by the addition of boric acid.[18] Precipitation is best carried out in the temperature range 40°–60°C., since at higher temperatures some molybdic oxide may precipitate; in the presence of arsenic and tetravalent vanadium the precipitation may with advantage be made at lower temperatures. Frey,[11] however, states that if precipitation is carried out below 65°C. an ammonium 9-molybdophosphate is precipitated; at temperatures higher than 65°C. ammonium 12-molybdophosphate is formed; a recent study of precipitation conditions has also been made by Archer *et al.*[19] Pentavalent vanadium should first be reduced with ferrous sulphate[20] or hydrazine hydrochloride before precipitation of the molybdophosphate. Silicon and tungsten are best removed as insoluble oxides and filtration (it may be necessary to examine the resultant silica or tungstic oxide for occluded phosphorus). In the presence of titanium, zirconium and bismuth it is preferable to fuse any insoluble residues with sodium carbonate and extract the sodium phosphate with distilled water. Organic materials should be decomposed by wet oxidation,[21-4] Parr bomb fusion[25] and, possibly, in selected cases by dry ashing.[26-7]

In view of the uncertain composition of ammonium molybdophosphate it is preferable to dissolve the precipitate in ammonium hydroxide solution and, after acidification and the addition of magnesium and ammonium chlorides, to reprecipitate the phosphorus as magnesium ammonium phosphate hexahydrate by the slow addition of ammonium hydroxide solution.[28] Finally the precipitate is ignited at 1000°–1100°C. to magnesium pyrophosphate and weighed. It has been claimed that some molybdenum is entrained by this procedure, but is volatilized almost completely if the ignition is carried out in an electric muffle.[29] Alternatively, after dissolution of the molybdophosphate in ammonium hydroxide solution and the addition of ammonium chloride and ammonium acetate as buffers, lead molybdate[30-1] may be precipitated by the addition of lead chloride. After filtration the precipitate is ignited at a temperature not exceeding 650°C. and weighed as lead molybdate. Other suggested transformations have been to molybdyl oxinate[32] and chloropentamminechromic tetrathiomolybdate.[33]

The prior precipitation of ammonium molybdophosphate serves to separate the orthophosphate from the many elements which are precipitated from ammonium hydroxide solution. Many of these elements, including calcium, iron, aluminium, tin, vanadium and titanium, are, even when present in considerable quantities, complexed by citric acid, whereas magnesium is only slightly complexed, thus permitting the direct precipitation of magnesium ammonium phosphate.[34] Calcium, strontium, barium, lead, copper, cadmium, zinc, nickel, cobalt and manganese can be complexed with ethylenediaminetetraacetic acid (EDTA),[35-7] again enabling a direct estimation of the phosphorus to be made. Přibil[35] recommends the substitution of Tiron (pyrocatechol-3:5-disulphonic acid) for EDTA if the solution contains aluminium, chromium, bismuth, antimony, tin, ferric iron, uranium, titanium or beryllium. In the direct method any pentavalent arsenic present will be precipitated as magnesium ammonium arsenate[38] and the acid solution must be treated with ammonium bromide to volatilize the arsenic. It is preferable in most cases (almost always in those cases where citric acid is used as the complexing agent) to dissolve the first precipitate of magnesium ammonium phosphate in hydrochloric acid and reprecipitate,[39-41] since the first precipitate is seldom pure and often contains the trimagnesium phosphate. Polyphosphates have been found to give rise to more phosphorus in the magnesium ammonium phosphate than that corresponding to the monophosphate content of the original solution.[42] It has been claimed,[43-4] and to some extent disputed,[45] that the addition of ammonium acetate prior to the final precipitation helps to give a crystalline precipitate. Saint-Chamant and Vigier[46] describe a method in which magnesium ammonium phosphate is precipitated by the slow evolution of ammonia resulting from the reaction of ammonium chloride and monoethanolamine. The crystals so formed are large and easily washed and only one precipitation is necessary. All these direct methods are capable of giving good results, largely due to compensation of errors,[47] but in all cases the ignition of the final precipitate should be conducted at a low temperature until all carbon is removed, otherwise the pyrophosphate is slowly reduced and phosphorus volatilized.[48] Other metal ammonium phosphates, amongst which are uranyl,[49] manganese[45,50] and zinc[45] ammonium phosphates, have been used to determine orthophosphate gravimetrically.

Quinoline molybdophosphate has a number of advantages over ammonium molybdophosphate as a suitable precipitate for the determination of orthophosphate. It is less soluble, of constant composition and free from occluded or adsorbed impurities apart from a small quantity of neutral contaminant, probably water, which is driven off when the precipitate is heated to 200°–250°C. The method,[51] in its original form, depended upon the formation of molybdophosphoric acid in a solution free from ammonium salts, followed by its precipitation as a salt of the weak base quinoline. It was later modified[52] to overcome the interference of silica by the addition of citric acid, which forms a stable complex with molybdic acid and prevents its reaction with silicic acid. The interference of ammonium salts is overcome in a similar manner. After heating to 200°–250°C. the quinoline molybdophosphate is weighed.[53-4] Calcium, magnesium, iron, aluminium and alkali salts are without effect on the results.

A similar method to the above is the precipitation of the oxine molybdophosphate.[53-9] The thermal decomposition of this compound was investigated by Duval[60] who reported a di-hydrate stable from 176–225°C., more or less in agreement with Berg,[56] who concluded that the dried precipitate was a dihydrate:

$$3C_9H_7ON.H_7[P(Mo_2O_7)_6],2H_2O$$

Wendlandt and Brabson in a re-investigation[61] stated that the compound begins to lose water at 60°C. giving a weight plateau at 85°–285°C. which corresponds to the anhydrous compound $3C_9H_7ON.H_3(PMo_{12}O_{40})$; above 285°C. some decomposition occurs giving another plateau at 335°–375°C., which corresponds closely to the 1-oxine compound. Finally, a plateau corresponding to the oxide $24MoO_3,P_2O_5$ begins at 470°C. They conclude that washing with ammonium nitrate may account for the accelerated decomposition of the experimental material of Duval and state that phosphorus may be determined by this method if the precipitate is dried at 140°C. The precipitate is said to be free from contamination, to have a high molecular weight and low phosphorus content, thus making it suitable for gravimetric analysis.[59] Another weak base which has been used to form a salt with molybdophosphoric acid is strychnine.[62-4] The resultant strychnine molybdophosphate also has a high molecular weight and low phosphorus content. It can be dried to constant weight. The quinine molybdate complex has also been used[65] as has the 1,2-dimorpholinoethane complex.[66]

A number of metal phosphates may be used to determine orthophosphate gravimetrically. Of these, bismuth phosphate may be precipitated from nitric acid solution by the addition of bismuth nitrate.[67-71] Calcium, iron, aluminium, magnesium, manganese and cobalt do not interfere. The precipitate may be either ignited at 700°–800°C. and weighed as anhydrous bismuth phosphate or filtered on a Gooch crucible, dried in vacuum, and weighed as $BiPO_4,\frac{1}{3}H_2O$. Lead phosphate may be precipitated from acetic acid/sodium acetate solution by the addition of lead acetate. After being heated to 600°–700°C. the lead phosphate is weighed. It is claimed for this method that it is as accurate as the molybdophosphate and magnesium pyrophosphate methods.[72] Zirconium oxychloride has been used as a precipitant for the mono- and di-zirconium phosphates.[73] Both mercury[74] and silver[75-6] phosphates may be dried and weighed. In both cases iron and aluminium interfere, but nitrate, sulphate, chloride, calcium and magnesium ions are without effect on the mercury phosphate method.

Numerous gravimetric micro and semi-micro methods have been developed from the macro procedures. The high molecular weight and low phosphorus content of the ammonium,[77] strychnine,[62, 78-9] quinoline[80-2] and oxine[83] molybdophosphates make them eminently suitable for this purpose and they have been so used. The separation of phosphorus by precipitation as the molybdophosphate and subsequent conversion to magnesium ammonium phosphate has also been used on a micro scale.[84] A semi-micro method has been described in which the phosphorus is precipitated as nitratopentammine cobaltidodecamolybdophosphate by the addition of nitratopentammine cobaltinitrate and alkaline sodium molybdate.[85] Advantages claimed are speed and the use of a low conversion factor.

### VOLUMETRIC

Orthophosphoric acid is tribasic and may be titrated with many bases to the mono- and di-stages, which occur at pH 4·5 and 8·55 respectively. The third acid group cannot be titrated directly, since the ionization constant is so small ($3{\cdot}6\times10^{-13}$).[86] Conversely the salts of orthophosphoric acid may be titrated with many acids. Numerous indicators have been recommended for these titrations[87-9]; one of the best is that of Peck.[90] Sodium chloride should not be present in the titration of the monobasic acid since its presence increases the hydrogen ion concentration of primary phosphate, but its presence is advantageous in the titration of the dibasic acid to phenolphthalein, since it represses the hydrolysis which causes the colour change to occur early.[91] It should also be noted that titration with alkali between the mono- and di-stages cannot be carried out accurately in the presence of ammonium ions. Variable amounts of ammonia are evolved during such titrations and the ammonium ion should be completely eliminated by boiling with excess alkali. The solution can then be titrated with acid to the di-stage then to the monosodium phosphate end-point. The presence of various cations causes dissociation of the ordinarily weak terminal hydrogen atoms; this results in a significant shift of the pH titration curve.[92-3] Potassium ferricyanide and potassium cobalticyanide are said to complex certain cations that are likely to form insoluble phosphates and liberate hydrogen ions.[94] By titrating between and to these stages many compounds and mixtures may be analyzed, e.g. boiler compounds, cast iron and organophosphorus compounds,[95] mixtures of tri- and di-sodium phosphate,[96] phosphoric acid,[97-8] phosphoric acid and ammonium, sodium and calcium phosphates in the presence of one another and of a strong acid or base.[99] The method is also applicable to the analysis of superphosphates.[100-1]

The third acid group may be titrated indirectly by the addition of neutral calcium chloride at the di-stage. It is probable that in the cold solution there is an initial partial precipitation of calcium monohydrogen phosphate (1) $Na_2HPO_4 + CaCl_2 = CaHPO_4 + 2NaCl$ which in solution or suspension is unstable and is in equilibrium with mono- and tricalcium phosphate[102-4]:

$$(2)\quad 4CaHPO_4 \rightleftharpoons Ca(H_2PO_4)_2 + Ca_3(PO_4)_2 \downarrow$$

Since tricalcium phosphate is very insoluble above pH 7 it precipitates from the alkaline solution, and thus the solution again becomes acid. On further titration to pH 8·5 the monocalcium phosphate is completely converted to the tricalcium salt: (3) $3Ca(H_2PO_4)_2 + 8NaOH = Ca_3(PO_4)_2 + 4Na_2HPO_4 + 8H_2O$. The net effect of stages 1 to 3 is the equation $2Na_2HPO_4 + 3CaCl_2 + 2NaOH = Ca_3(PO_4)_2 + 6NaCl + 2H_2O$. By this means mixtures of phosphoric acid, mono- and di-alkyl phosphoric acids and the trialkyl phosphate may be evaluated[102]; the neutral compound is found by difference. In the titration of acid extracts of phosphates the overtitration which would result from the presence of alkaline earths may be avoided by adding an excess of calcium chloride and titrating in effect the second and third hydrogen ions.[105-6] Cerium[107-8] and silver salts[109-11] have also been used to liberate hydrogen ion from phosphoric acid. If solutions of tricalcium phosphate are boiled in the presence of hydroxyl ion, hydroxy-apatite $[3Ca_3(PO_4)_2,Ca(OH)_2]$ is formed[112] and methods based on the reaction $6H_2PO_4^- + 10Ca^{2+} + 14OH^- = 3Ca_3(PO_4)_2,Ca(OH)_2 + 12H_2O$ have been used to determine phosphate.[113-4]

If orthophosphoric acid is titrated with calcium hydroxide solution all three hydrogen ions are titrated but only two end-points are found. The first inflection corresponds to the formation of monocalcium phosphate after which, on addition of further calcium hydroxide, calcium monohydrogen phosphate begins to form, and this decomposes above pH 5·5 as already described; the second inflection corresponds to the total precipitation of tricalcium phosphate.[103-4] The decomposition of calcium monohydrogen phosphate at lower pH values is slow and the neutralization curve may show irregularities if its titration is carried out in the normal manner; the orthophosphate concentration is also said to influence the composition of the precipitate formed.[115] The titration has found practical application in the analysis of superphosphates.[116]

If orthophosphoric acid is titrated with potassium iodide/iodate solution, one molecule of acid will liberate two atoms of free iodine.[117] Bromate has replaced iodate in a variant of this method.[118]

Many, if not all, of the gravimetric methods for the determination of orthophosphates may be finished volumetrically. Ammonium molybdophosphate may be dissolved in a known excess of sodium or potassium hydroxide and the excess back-titrated[119-23]:

$$2(NH_4)_3[PMo_{12}O_{40}]+46NaOH = 23Na_2MoO_4+(NH_4)_2MoO_4+2(NH_4)_2HPO_4+22H_2O$$ [2]

The method is subject to all the disadvantages previously mentioned, and in addition (if the determination is carried out as in the original method[124-5] and the precipitate is washed with water) has the disadvantage of losses occurring through the appreciable solubility of the molybdophosphate and its tendency to pass through the filter. Some of these effects may be reduced by washing the precipitate with potassium nitrate solution (or ammonium nitrate solution in which it is less soluble) but some error may be introduced by the occurrence of cationic exchange. The precipitate is liable to decomposition by hydroxyl ions and the presence of ammonia affects the phenolphthalein used to detect the end-point.[4] Attempts have been made to overcome this by evaporating the alkaline solution, or more advantageously by the addition of formaldehyde to form hexamine from the ammonia: 26 g.-equivalents of sodium hydroxide decompose 1 g.-equivalent of the triammonium salt in these cases. If the precipitate has been washed with potassium nitrate and cationic exchange has occurred, the use of these methods can lead to error owing to the variable amount of sodium hydroxide which will be consumed.[2-3,9] In the analysis of metallurgical samples where an oxidative attack converts phosphides to phosphate suitable for precipitation as molybdophosphate followed by a titrimetric finish, the use of a comparative standard alloy is preferred to using the method in an absolute manner, in order to eliminate some of these and other errors. This use of standard steels is based upon the following assumptions: the phosphorus content of the standard steel is known; each subsequent steel test sample will behave as the standard; the same number of the same errors will occur in the same way each time; and, finally, that a relatively complicated procedure using an empirical standard is more precise and accurate than the use of a relatively simple procedure using primary or secondary chemical standards. Methods have been described in which a precipitate of ammonium molybdophosphate containing acetone is formed[9,13,126]; the amount of sodium hydroxide consumed in the titration of these precipitates appears to be variable. Metals which interfere in the gravimetric procedures will of course also interfere in the volumetric finish, although this volumetric procedure has been applied in the presence of titanium[127] and vanadium.[128-9]

Methods have been described based on the dissolution of the ammonium molybdophosphate in sodium or ammonium hydroxide solutions, followed by reduction of the molybdenum using zinc and hydrochloric acid, lead, zinc, bismuth amalgams, silver or mercury and subsequent titration of the reduced molybdenum with ammonium vanadate,[130-1] ceric sulphate,[132] potassium permanganate[133-4] or methylene blue.[135] In another method,[136] ammonium sulphomolybdophosphate is precipitated, dissolved in sodium hydroxide solution, reduced by means of zinc and titrated with permanganate in the presence of benzidine. In view of the uncertainties associated with the formation of the molybdophosphate, such as the co-precipitation of molybdic oxide, it is questionable whether these procedures offer any marked advantages.

Magnesium ammonium phosphate may be dissolved in hydrochloric acid, a known excess of EDTA or its disodium salt added, and the excess titrated with standard magnesium solution using Eriochrome Black T as indicator.[137-40] Alternatively, the phosphate may be precipitated as magnesium ammonium phosphate by the addition of a known excess of magnesium chloride with ammonium chloride and ammonium hydroxide; after filtration and washing of the precipitate, the excess of magnesium in the filtrate is then determined by titration with EDTA or its disodium salt.[141-2] Another variant is to titrate the orthophosphate directly with standard magnesium solution using Eriochrome Black T as indicator.[143-6] The solution should be at pH 10 before commencement of the titration. It has also been claimed that orthophosphate may be titrated directly with the disodium salt of EDTA in the presence of Eriochrome Black T and sulphosalicylic acetate.[147] Of a number of methods critically reviewed by Eschmann and Brochon,[148] the compleximetric titration of the magnesium in the magnesium ammonium phosphate obtained by the Saint-Chamant and Vigier method[46] was considered to be the best.

Of the other metal ammonium phosphates, the uranyl salt can be reduced to the trivalent state using zinc amalgam, or to the tetravalent state with bismuth amalgam or aluminium and titrated back to the uranyl condition with potassium permanganate or dichromate.[149-50] The manganous ammonium phosphate may also be dissolved in acid and titrated with potassium permanganate at 80°–90°C.[151] Zinc ammonium phosphate may be converted into zinc oxalate by treatment with oxalic acid and subsequently titrated with potassium permanganate.[152] Alternatively the precipitate may be dissolved in hydrochloric acid, neutralized with ammonium hydroxide and titrated with EDTA using Eriochrome Black T as indicator.[153]

Amongst the best of the volumetric methods is the quinoline molybdophosphate procedure of Wilson.[51-2] In this procedure the precipitate is dissolved in a known excess of sodium hydroxide and the excess back-titrated:

$$(C_9H_7N)_3H_3(PMo_{12}O_{40}) + 26NaOH = Na_2HPO_4 + 12Na_2MoO_4 + 3C_9H_7N + 14H_2O.$$

The advantages of this method over the analogous volumetric ammonium molybdophosphate method lie in the greater insolubility of the precipitate, its freedom from ammonia and its consistent composition. A number of applications of this method have been described[154-5] including its application to the determination of phosphate in the presence of vanadium[156] and to the combined determination of phosphorus and arsenic.[157]

Oxine molybdophosphate, after dissolution in hydrochloric acid, may be titrated with standard bromate/bromide solution, and the method has been used to determine phosphate.[158-63] In another variant[164] the excess oxine in the filtrate following the precipitation of the oxine molybdophosphate has been determined[165] and the phosphate content deduced. In another the phosphate solution is titrated with an oxine–molybdate solution. These methods, although novel, would seem to have little advantage over the quinoline procedures, apart possibly from the last which may be rapid, although not very accurate.

Procedures involving the precipitation of metal phosphates have their volumetric variants. Orthophosphate can be titrated directly with a bismuth salt using potassium iodide as indicator; excess of bismuth is indicated by the formation of the red bismuth oxy-iodide.[166] In one method[167] the maximum turbidity due to the precipitation of bismuth phosphate is used to detect its end-point when titrating orthophosphate with bismuth oxy-perchlorate; in another[168] the end-point is indicated by the formation with thiourea and excess titrant of a bright yellow complex. A known amount of a bismuth salt may be added to an orthophosphate solution and the excess determined by titration with EDTA,[169-72] using pyrocatechol violet[169-70,172] or xylenol orange[171] as indicator; organic complexing agents interfere.[173] High accuracy is claimed for the titration of orthophosphate with lead acetate in an acetic acid buffer, using dithizone to detect the end-point,[174] and with lead nitrate using Eriochrome Black T as indicator.[175] Mercuric phosphate may be dissolved in dilute nitric acid and the mercuric ion titrated with potassium thiocyanate, affording a measure of the phosphate content; this method is said to be unaffected by nitrate, sulphate, chloride, calcium or magnesium ions but gives low results in the presence of ferrous, ferric and aluminium ions.[74] Other possible methods include the precipitation of silver phosphate and subsequent determination of the silver content of the precipitate by Volhard's method,[75,176-7] or in one case[178] by titration of the precipitate in the presence of ceric ion and starch with potassium iodide. Initially silver iodide is formed; excess of potassium iodide reacts with the ceric salt, liberating free iodine which, by forming starch iodide, marks the end-point. Ceric sulphate has also been used to precipitate ceric phosphate and the excess determined in the filtrate with ferrous sulphate[179]; cerous salts have been used in a similar reaction except that excess is detected by the use of Eriochrome Black T.[180] Lanthanum ion precipitates phosphate preferentially in the presence of calcium and barium and the excess of lanthanum can be determined compleximetrically.[181]

Benzidine phosphate is sufficiently insoluble in neutral or weak acetic acid solution to enable orthophosphate to be determined. The benzidine phosphate is titrated with sodium hydroxide after its precipitation and filtration. The method has been applied to superphosphate analysis, and it is claimed that it enables a distinction to be made between phosphate and sulphate.[182]

If orthophosphate in the presence of hydrochloric acid is shaken with ethyl ether and an alkali-metal molybdate,[183] or with a mixture of butyl ether and methyl ethyl ketone and an alkali-metal molybdate,[184] a complex is formed which is insoluble in both the aqueous and organic phases. By measuring the volume of this insoluble liquid phase a measure of the phosphate content of the original solution can be obtained.

Several micro- and semi-micro procedures for the volumetric determination of orthophosphate are known. These are based on macro-procedures such as alkali titration of ammonium molybdophosphate,[185–6] with variants such as determination of the molybdenum content of the precipitate by reduction and titration of the reduced solution with an oxidizing agent,[187] or estimation of the nitrogen content by a micro-Kjeldahl procedure.[188] Strychnine molybdate has also been used to precipitate orthophosphate and the carbon content of the precipitate determined by the gas volumetric method of Van Slyke.[189] Magnesium ammonium phosphate precipitation has also been used on a micro and semi-micro scale, and the precipitate titrated compleximetrically.[190–1] Heterometric titrations have been used for the determination of phosphorus on the micro scale.[192]

### SPECTROPHOTOMETRIC

A yellow hue develops when excess of molybdate solution is added to an acidified solution containing orthophosphate ions. The colour may be attributed to the formation of the 12-molybdophosphate anion[193–4] which exists only in acid solution.[195] The yellow solution gives an absorption maximum at 332 mμ[196] and at this wave-length obeys Beer's Law up to a concentration of 1 p.p.m. of phosphorus and is thus suitable for the spectrophotometric determination of phosphorus. A large excess of molybdate over the stoicheiometric amount is necessary for maximum colour development, and since the molybdate ion (which appears to have an absorption maximum around 210 mμ) absorbs strongly in the molybdophosphate absorption region, it is necessary to read the absorption at 380–420 mμ if higher concentrations are to be determined.[197] At the higher wave-length, concentrations of up to 25 p.p.m. of phosphorus still obey Beer's Law. The pH of the solution should lie between 0·5 and 1·2 depending upon the acid used which may be sulphuric, hydrochloric or nitric.[197] The presence of other ions which form heteropoly anions such as silicon, germanium, arsenic and tungsten will cause interference and these must be removed, as must ferric ions which are yellow-coloured (this interference can be minimized by the use of a test solution without added molybdate in the reference cell) and bismuth which causes a change in hue.[197] Ammonium salts are said to reduce the intensity of the colour developed but this does not preclude the use of ammonium molybdate, as the resultant ammonium molybdophosphate is sufficiently soluble to allow its utilization to determine low concentrations of orthophosphate spectrophotometrically or colorimetrically.[198] It has been mentioned that a large excess of molybdate must be present; this has the effect of reducing the sensitivity of the method (the molar extinction coefficients in litres per mole cm. for phosphorus by this procedure are 14,000 at 332 mμ, 2540 at 380 mμ, 1330 at 400 mμ and 750 at 420 mμ). Since at the longer wave-lengths measurement is made on the slope of the absorption curve, the reproducibility must also suffer: for this reason (and because silicon and other elements form heteropoly anions) it is often preferable to use other methods.

The structure of the heteropoly acids is 'open' and can accommodate numerous water or other solvent molecules[199]; thus a molybdophosphate–acetone complex is known and methods have been developed utilizing this fact.[200-1] The absorption maximum for the complex occurs at 320 mμ and, at this wave-length, the molar extinction coefficient in litres per mole cm. for phosphorus is 19,800: the procedure is therefore rather more sensitive than methods based on molybdophosphate alone. Much that has been said before concerning the excess of molybdate which is necessary, applies with equal force to this procedure.

Molybdophosphoric acid may be extracted with many solvents and by this means can be separated from the necessary excess of molybdate ion and also, by choice of solvent and acidity conditions, from other heteropoly-acids. Esters, ketones, aldehydes and ethers are good solvents; carbon disulphide, carbon tetrachloride, chloroform, benzene and toluene are not.[202] Keggin[203] has stated that oxygen-containing liquids are good solvents. Of the esters, *n*-butyl acetate is very selective for molybdophosphoric acid[204]; *iso*-amyl acetate has also been used selectively to extract molybdophosphoric acid from molybdosilicic and molybdoarsenic acids.[196] *n*-Butanol, either alone,[205] or in chloroform,[204, 206-7] is much favoured as an extractant. The selectivity decreases and its sensitivity increases as the concentration of *n*-butanol increases. In 20% v/v butanol/chloroform the molybdophosphoric acid shows an absorption maximum at 310 mμ and the extinction coefficient in litres per mole cm. for phosphorus is 25,400. *iso*-Butanol in chloroform has also been used to extract molybdophosphoric acid from a mixture of molybdoarsenic, molybdosilicic and molybdogermanic acids in 0·14 N. nitric acid solution.[208] Other methods have been described using ethyl acetate,[209] butyl acetate[210-1] and amyl acetate[212] as extractants. In nearly all cases, however, butanol/chloroform is the preferred solvent, the method being of high sensitivity and, with suitable control of conditions, of high selectivity.

Another sensitive method is that of Denigès,[213] based upon the reduction with stannous chloride of the molybdophosphate ion to 'molybdenum blue' (first proposed by Osmond[214]). As well as the papers of general interest[215-7] there are those describing specific applications of the method to the determination of phosphorus as phosphate in blood,[218] phosphorus acids,[219] cerebrospinal fluid,[220] oil,[221] soils,[222] air,[223] soil extracts,[224-5] organophosphorus compounds,[226] sea water,[227] steel (both manually[228] and automatically[229]) and acetylene.[230] Reducing agents other than stannous chloride have been used in some of the subsequent developments of the method: 1-amino-2-naphthol-4-sulphonic acid,[231-40] hydroquinone,[241-8] ascorbic acid,[249-55] hydrazine sulphate,[256-61] *p*-methylaminophenol,[262-9] 2:4-diaminophenol hydrochloride,[270-1] thiourea,[272-4] ferrous,[275-8] sulphite ion,[279] thiosulphate ion,[280] pyrogallol,[281] potassium iodide[282] and *p*-semidine.[283] It is claimed[284] that higher values of molar extinctions are obtained with a number of reductants if *o*-dianisidine molybdate is used instead of ammonium molybdate. A very comprehensive list of reductants, acidity conditions and applications, is given by Jean[285]; there are also other reviews.[286-8] Colourless molybdenum trioxide when partially reduced in strongly acid solution yields an unstable 'blue' which disappears on dilution. A 'blue' colour is reformed and stabilized by the addition of orthophosphate. Several methods are based on this procedure[289-99] and it is claimed[300] that the absence of reducing agents in the final solution leads to a more stable 'blue'. The composition of the reduced molybdophosphate is uncertain; a formula which appears frequently in the literature is $(MoO_2.4MoO_3)_2H_3PO_4$, but it is also claimed that the complex contains two compounds: I, $H_3PO_4.10MoO_3.Mo_2O_5$ and II, $H_3PO_4.8MoO_3.2Mo_2O_5$. (A mixed reducing agent of sodium metabisulphite, sodium sulphite, 1-amino-2-naphthol-4-sulphonic acid and sodium-1-aminonaphthalene-4-sulphonate is claimed to reduce molybdophosphate to $H_3PO_4.10MoO_3.Mo_2O_5$ in 20 min.[301]) The 'blue' has an absorption maximum at 830 mμ with an inflexion at 640 mμ and at 830 mμ the molar extinction in litres per mole cm. for phosphorus is 25,700. The reaction is not specific for phosphorus since other elements which form heteropoly acids with molybdenum also give blue compounds on reduction, as does the molybdate reagent itself. At acid concentrations of the order of 0·35 N. and above, the excess molybdate reagent will not be reduced.[302-5] Where stannous chloride is used as a reductant it is claimed that the presence of potassium chlorate prevents the reduction of excess molybdate reagent.[306-7] Molybdosilicate, molybdoarsenate and molybdophosphate are formed at low acidities[308] and at such acidities all will be reduced. However, having formed the heteropoly compounds, if the acid concentration is then raised sufficiently, only molybdosilicate is reduced. On the other hand, at intermediate acidities only molybdophosphate and molybdoarsenate are formed and may be reduced.[309] Thus by controlling the acidity at the formation and reduction stages some selectivity may be achieved.[310-11] The acidities necessary to achieve this selectivity will vary with the concentration of the molybdate reagent and with the reducing agent chosen, and should be determined for each method.[216, 312-3] The interference of arsenic may be overcome by reducing it to its arsenious condition, in which state it does not form a heteropoly compound[314]; there are also differences in rates of reduction[315-6] and types of reaction with certain reducing agents.[317] Another method of overcoming the interference of other heteropoly compounds is to use complexing agents such as tartaric acid[318] which inhibit the 'moly-blue' complexes of silica and arsenic; these have been discussed in some detail by Jean.[285-6] Extraction with organic solvents followed by measurement of the phosphorus as 'moly-blue' in the aqueous phase has also been used to achieve selectivity.[319-21] The effects of a number of cations and anions on the determination of phosphorus by 'moly-blue' have been discussed[302, 322]: barium, lead, mercury, silver, strontium and zirconium are said to give precipitates; bismuth, cadmium, chromium, copper, iron and zinc are said to form complexes which bleach the colour. Ferric iron interferes by virtue of its oxidizing action and must be reduced.[304, 308, 310, 323] Fluoride inhibits the formation of molybdophosphate[324] and trichloroacetic acid enhances the colour.[325]

Mention should be made of the procedures whereby molybdophosphoric acid is extracted by various solvents and then reduced to the 'blue' which is measured in the organic phase.[326-33] These procedures combine high selectivity with high sensitivity and freedom from element interference. The molar extinction coefficient in litres per mole cm. for phosphorus at 800 mμ is 29,800.

Misson[334] proposed the use of molybdivanadophosphate for the determination of phosphate. The orange-yellow complex is formed when a soluble vanadate, followed by a soluble molybdate, is added to an orthophosphate solution. The complex (formulated $(NH_4)_3PO_4.NH_4VO_3.16MoO_3$ by Misson), is written $P_2(V_2O_5)(Mo_2O_7)_{11}$ by Maksimova and Kozlovskiĭ,[335] but it would appear that the exact nature of the compound is in doubt. The colour is stable for at least 14 days,[336-7] and the method has been used to determine phosphorus in steels,[338-43] iron ores,[336, 344] organic phosphates,[345-7] calcium compounds,[348] fertilizers,[349] vanadic acid,[350] petroleum products,[351] soils,[352] tributyl phosphate,[353] uranium ores,[354] tungsten ores,[355] basic slag[356] and plant substances.[357-8] It is similar to the molybdophosphate procedure in that the absorption maximum occurs where the reagents are absorbing strongly and for this reason measurement of the colour is often made between 400 and 450 mμ on the slope of the absorption curve with a resultant loss in sensitivity and reproducibility. The molar extinction for phosphorus in litres per mole cm. at 420 mμ is 1500. Recent work has shown that the absorption maximum lies between 315 and 340 mμ.[359, 360] The acidity of the solution should lie between 0·2 N. and 1·6 N,; colour development is slower at higher acidities.[337] Sulphuric, nitric, hydrochloric and perchloric acids behave much alike when used in adjusting the acid concentration. The stoicheiometric ratios of vanadate to phosphate and molybdenum to phosphorus are approximately 1 : 1 and 14 : 1[337, 359] respectively and a 50% excess of these reagents should suffice. The vanadate must be added before the molybdate, otherwise the yellow molybdophosphate will be formed (although mixed reagents have been used).[361] Temperature effects have been reported.[343, 362] Ferric salts interfere since in solution they absorb in the same region as the complex; silica interferes in a similar manner by the formation of molybdosilicate. Both interferences may be overcome by a preliminary fuming with perchloric acid; ferric salts are decolorized and silica is rendered insoluble.[336] Ions which complex molybdenum should be removed.[363] Arsenate gives a similar colour to phosphate. The effects of these and other diverse ions have been dealt with in a number of papers,[337, 359] which, together with papers dealing with conditions for the formation of the complex, have been reviewed by Jean.[285-6] One of the most important applications of the method is in the determination of relatively large quantities of phosphate by differential spectrophotometry.[359] In this application the comparatively low sensitivity and high stability are advantageous. The method has been used in an automated procedure.[364]

Molybdivanadophosphoric acid can be extracted into an organic solvent such as *iso*-amyl alcohol[365-7] or methyl *iso*-butyl ketone[368] and in these solvents it has a molar absorptivity similar to that of the complex in aqueous solution. It is possible that such a treatment offers a method of overcoming the interference by coloured ions.

Molybdophosphate has been reduced with benzidine in weakly acid solution to molybdenum blue[369]; in this case the colour is augmented by the formation of benzidine blue. The molar extinction coefficient for phosphorus in litres per mole cm. at 885 mμ is 11,600. In another application benzidine molybdophosphate is precipitated. After filtration, hydrazine sulphate solution is added to the precipitate and, after removal of the benzidine sulphate, molybdenum blue remains.[370]

Hydrazine hydrochloride and ammonium oxalate added to molybdophosphate in ammonium hydroxide solution give a reddish-orange colour which obeys Beer's Law. The colour is attributed to a quadrivalent molybdenum-oxalate complex.[371] $\epsilon_{425\,m\mu}$ is 984 litres mole$^{-1}$ cm.$^{-1}$ for phosphorus.

Strychnine molybdophosphate after dissolution in sodium hydroxide solution has been examined between 350 and 400 mμ.[372] Clearly, the absorption of the molybdophosphate anion is measured. In another application the strychnine molybdophosphate, dissolved in sodium carbonate solution, is reduced with phenylhydrazine and the wine-red colour of the reduced molybdenum measured.[373] $\epsilon_{497\,m\mu}$ is 105,000 litres mole$^{-1}$ cm.$^{-1}$ for phosphorus.

The decrease in intensity of a ferric salicylate complex (measured at 550 mμ) in the presence of phosphate ion is the basis of a method for the determination of phosphorus in soils and non-ferrous metals.[374] $\epsilon_{550\,m\mu}$ is 269 litres mole$^{-1}$ cm.$^{-1}$

Lueck and Boltz[375] describe a method in which molybdophosphoric acid is extracted with an ether/*iso*-butanol mixture followed by a retrograde extraction with a basic buffer solution which results in the decomposition products being transferred to the aqueous phase. The extinction of the basic molybdate solution is then measured at 230 mμ. It is claimed that a value for $\epsilon_{230\,m\mu}$ of 57,400 litres mole$^{-1}$ cm.$^{-1}$ can be achieved. A number of ions were studied for interference effects; of these, arsenate, arsenite, germanate, nitrite and silicate must be absent.

A mixed ammonium molybdate/methylene violet reagent has been used as a precipitating agent to determine phosphate in blood. The precipitate is dissolved in acetone and the deep purple colour compared with standards.[376]

Lanthanum chloranilate reacts with phosphate in a solution buffered at pH 7 to give lanthanum phosphate and release chloranilic acid, the absorption of which is measured at 530 mμ.[377] A value of 269 litres mole$^{-1}$ cm.$^{-1}$ for $\epsilon_{530\,m\mu}$ is given. Wynne, Burdick and Fine remove interfering cations and anions with strongly acidic or basic ion exchange resins before colour development.[378]

A sensitivity far higher than any method so far discussed is claimed for a procedure in which safranine molybdophosphate is extracted with acetophenone and the extinction measured at 532·5 mμ.[379] A value for $\epsilon$ for phosphorus of 190,000 litres per mole cm. at 532·5 mμ is reported. The extraction is quantitative at pH 1·5, but arsenate, arsenite and vanadate interfere. Beer's Law is not followed, hence the molar absorptivity quoted is obviously an average figure. The following values have been obtained in the authors' laboratory; $\epsilon^{-1}{}_{\text{molar}}$ (20°C., 1·24 μg P) = 140,000, $\epsilon^{-1}{}_{\text{molar}}$(25°C, 1·24 μg P) = 115,000 and $\epsilon^{-1}{}_{\text{molar}}$(25°C. 1·55 μg P) = 132,000.

### NEPHELOMETRIC AND TURBIDIMETRIC

A number of nephelometric[380-6] and turbidimetric[387-9] methods have been described. They all depend upon the formation in acid solution of molybdophosphates of alkaloids such as strychnine. A comparison of the respective merits of colorimetric and nephelometric methods of determining phosphate has been made.[390]

### ION EXCHANGE SEPARATIONS

Some phosphatic minerals can be brought into solution by agitating their aqueous suspensions with a cation exchange resin in its 'acid' form. By this treatment the cations are held on the resin and the orthophosphate anion is liberated as orthophosphoric acid. After removal of the resin by filtration the acid can be titrated with alkali.[391-3] Other materials require prior treatment with acid to effect solution, in which case the acid solution is passed down an exchange column and, after neutralization of the dissolving acid, the phosphoric acid is titrated between pH 4·6 and pH 9.[394-404] It is said that ferric ion should first be reduced to the ferrous state.[405] Vanadium should also be reduced.[406-7] It must be noted that the method is rarely as simple as this description would suggest. Many minerals require an alkali fusion to effect solution; others leave siliceous residues which after removal of the silica with hydrofluoric acid also require a fusion to dissolve the metal oxides remaining. In these cases the ion exchange column has to be increased in size to accommodate the extra sodium or potassium ion, greatly extending the time required for an analysis. Also the large quantity of acid other than phosphoric has to be neutralized, thus causing a marked salt effect on the end-point in the final titration. Other anions which would titrate have to be removed.[408] In general, if all the precautions are taken to obtain a result of reasonable accuracy, the time required is much greater than is required by other more precise methods. It must, however, be conceded that these ion-exchange methods might be useful where only moderate accuracy is required.

### RADIOMETRIC

Phosphorus in a material can be very accurately determined by irradiating a sample together with a known standard in the same flux density for the same time. The specific activities induced by the reaction $^{31}P(n, \gamma)^{32}P$ will be the same, so a comparison of activities will allow a determination of the mass of phosphorus in the sample.[409-20] After conversion of the phosphorus in the sample to orthophosphate by hydrolysis and/or oxidation, inactive phosphate is added as a carrier and the orthophosphate is isolated in a suitable form. After filtration and drying the activity is counted by means of a Geiger–Müller tube with associated apparatus, or by means of a scintillation counter. The method is sensitive, specific and independent of impurities in the reagents. In those cases where a prior separation is not necessary it can be non-destructive and is very rapid. On the other hand, there are limitations to the size of sample, since a measure of self-shielding may occur, or the sample may be larger than the region of highest flux. Heating may occur, necessitating the sealing of some samples. Side reactions may happen (e.g. $^{32}S(n,p)^{32}P$) while impurities in the reference standard may be disadvantageous to the use of the technique.

Isotope dilution analysis is a versatile method and depends on the determination of specific activity. A mass of active phosphate (or active precipitant) of known specific activity is added to an unknown mass of inactive phosphate. After equilibrating, a small portion of pure orthophosphate is isolated; the specific activity is measured and the phosphorus content of the unknown sample determined.[421-3] A variant of this method is one in which a sub-stoicheiometric amount of inactive precipitant is added to a solution containing inactive phosphorus and a known amount of active phosphorus. After removal of the precipitate the residual activity is counted.[424]

Active phosphorus ($^{32}_{15}P$) has been used to enable separated spots on chromatograms to be detected and the quantity of phosphate present to be determined by counting the activity of the spots.[425-7]

Use has been made of active phosphate as a tracer to study the efficiencies of gravimetric methods of determining and removing phosphate.[428-30]

Finally, mention should be made of radiochemical methods of tracing phosphorus in plant material.[431-4]

### ELECTROMETRIC

Many of the titrimetric methods discussed in a previous section can be performed potentiometrically, using various electrode systems in place of indicators. These methods include the titration of orthophosphoric acid and its salts with alkali or lime,[93, 435-7] precipitation of quinoline[438] or ammonium[439] molybdophosphate or magnesium ammonium phosphate,[440] followed by acid–alkali titration of the filtered precipitate. There are many other possible applications of the technique. This finish is particularly advantageous when dealing with coloured solutions, or when salt and/or solvent effects decrease the rate of change of pH (or e.m.f.) with titrant addition. In these cases it is difficult to detect end points with indicators. In general pH curves give more information than is obtainable by indicator titrations, as for instance when titrating dialkyl phosphates the presence of an inflexion on the pH curve before that due to the di-compound indicates the presence of monoalkyl phosphate.

Polarized bimetallic electrode systems and platinum indicator electrodes have been used to determine end points in the redox titration of the molybdenum content of molybdophosphate with titanous sulphate solution.[441] Platinum–calomel electrode combinations have been used in a similar procedure where stannous chloride solution has been used as the titrant.[442]

Potentiometric precipitation titrations have had their advocates; the excess of mercurous nitrate (following the precipitation of the phosphate) has been titrated potentiometrically with sodium oxalate solution.[443] Phosphate ion has also been titrated potentiometrically with mercuric nitrate solution[444] and with lead acetate solution.[445] Mention should also be made of the use of the silver electrode and silver/silver chloride reference electrode in argentometric titrations.[446-7] Lévy[448-9] used a system in which the e.m.f. of the titration cell is opposed to that of a potentiometer standardized to the e.m.f. of a reference cell containing the same ions. At the equivalence point the titration cell has the same potential as the reference cell.

A number of amperometric methods have been developed for the determination of phosphate. In these methods the decrease and/or increase of a polarographic wave, following the addition of titrant, is used to plot titration curves. In one of these methods molybdophosphate is extracted with *iso*-butanol, and after reduction with zinc amalgam, the molybdenum content is determined by titration with ferric chloride solution.[450] Direct amperometric titrations of phosphate have been made with ferrous ammonium sulphate,[451-2] uranyl acetate,[453-4] bismuth nitrate,[455] vanadyl sulphate,[456] and lead acetate solutions.[457] A method has been described in which a solution of hydroxyquinoline and ammonium molybdate is titrated amperometrically with phosphate solution.[458]

There are methods in which phosphorus is precipitated as metal phosphates or complex phosphates, and either the excess of precipitant or the metal content of the precipitate or the complex itself is determined polarographically by measurement of the wave height, thus affording an indirect measurement of phosphate content. These polarographic methods include the measurement of the wave height of the quinoline molybdophosphate complex,[459] the determination of the molybdenum content of molybdophosphate[460-1] and the determination of the excess of molybdate following the precipitation of molybdophosphate.[462-3] Finally, mention should be made of the polarographic determination of bismuth in bismuth phosphate[464] and excess of lead acetate following the precipitation of lead phosphate.[465]

Conductimetric titration techniques have also been used to determine end points as in the titration of phosphate with uranyl nitrate,[466] sodium hydroxide[467] and bismuth nitrate[468] solutions. Two interesting applications of this technique are the determination of both the 'ammonia' and 'phosphoric acid' contents of fertilizers by conductimetric titration of a single sample with sodium hydroxide solution[469] and the titration of phosphoric acid with bismuthyl perchlorate solution.[470] This last application is carried out in perchloric acid solution and it is claimed that good results are obtained in solutions containing magnesium, calcium, copper, zinc, nickel, ferrous iron, manganese, aluminium, small amounts of ferric iron, nitrate, chloride and silica.

High frequency titrations do not seem to have received much attention for phosphate titrations and one worker has reported peculiar results by this technique.[471]

Coulometric methods have been used to titrate molybdophosphate[472] and quinoline molybdophosphate[473] with electrolytically produced hydroxyl ions. The molybdenum content of molybdophosphate has also been determined coulometrically.[474]

## Condensed Phosphates

### GRAVIMETRIC

Pyrophosphate can be determined in the presence of orthophosphate by precipitation of barium phosphate, $Ba_3(PO_4)_2$, and barium pyrophosphate, $Ba_2P_2O_7$, with barium hydroxide solution.[475] The amount of precipitant consumed is determined by precipitating and weighing the excess of barium as barium sulphate. The total phosphorus is then estimated by an alternative procedure. From the two results the pyro content can be calculated. However, ortho, pyro, and triphosphate are incompletely precipitated by the barium ion; only the higher linear phosphates are precipitated quantitatively. This fact is used to determine cyclic metaphosphates in the presence of higher linear phosphates after removal of the lower linear polymers by anion-exchange chromatography.[476] Zinc pyrophosphate may be quantitatively precipitated at a pH of 3·8 from solutions containing ortho- and tri-phosphate.[477-9] The precipitation is said to be quantitative in the presence of triphosphate only if the ratio of pyrophosphate to triphosphate is $>1:9$ and the precipitate is allowed to stand for 12 hours, but accurate results are readily obtained when orthophosphate is the only other constituent.[480]

The barium and zinc precipitates are not particularly amenable to direct weighing and better precipitants for quantitative determination are the halide or nitrate salts of the hexammine cobalt complex. Pyrophosphate may be weighed as hexamminecobalt(III) monosodium pyrophosphate, $[Co(NH_3)_6]NaP_2O_7$, after precipitation from cold 5% ammoniacal solution.[481] Ortho, pyro and triphosphate may be determined as hexamminecobalt(III) phosphate tetrahydrate $[CO(NH_3)_6]PO_4,4H_2O$, precipitated at pH 12·3, hexamminecobalt(III) monohydrogen pyrophosphate $[Co(NH_3)_6]HP_2O_7$, precipitated at pH 7·9 and sodium hexamminecobalt(III) triphosphate $[Co(NH_3)_6]Na(P_3O_{10})_2$, precipitated at pH 7·9, with a claimed precision of ±2·5% for single components.[482] The formulae hexamminecobalt(III) monohydrogen phosphate $[Co(NH_3)_6]_2(HPO_4)_3$, precipitated at pH 11·8, and hexamminecobalt(III) dihydrogen triphosphate $[Co(NH_3)_6]H_2P_3O_{10}$, precipitated at pH 8·3–8·6, have also been quoted, [483] using similar precipitation and drying conditions. Tris(ethylenediamine) cobalt bromide has also been used as a precipitant for pyro- and tri-phosphate, forming tris(ethylenediamine) cobalt(III) monohydrogen pyrophosphate dihydrate $[Co(en)_3]HP_2O_7,2H_2O$ at pH 6·5–6·7 and tris(ethylenediamine) cobalt(III) dihydrogen triphosphate dihydrate $[Co(en)_3]H_2P_3O_{10},2H_2O$ at pH 3·4–3·5.[484] Tris(ethylenediamine) cobalt(III) chloride has been used as a selective precipitant for triphosphate [485] which is precipitated at pH 3·5; pyrophosphate does not interfere. At pH 6·5 pyrophosphate is precipitated with no interference from triphosphate. In neither determination is orthophosphate or trimetaphosphate precipitated. Weiser[486] maintains that the triphosphate precipitate may co-precipitate some pyrophosphate; a compensating method is suggested for overcoming this interference.

Benzidine is a non-specific reagent and will precipitate all phosphates. It has been used as a precipitant for long chain phosphates[487] after prior removal of the lower phosphates. Partial selective separations of condensed phosphates may be achieved using other amines dissolved in acetic acid solution: aniline, *p*-phenylenediamine, *m*-phenylenediamine, *m*-tolylenediamine, phenylhydrazine and piperazine precipitate only linear phosphates of fairly long chain; 2-naphthylamine will precipitate all phosphates except trimetaphosphate; and diaminobenzidine and *o*-tolidine will precipitate all phosphates except orthophosphate and trimetaphosphate.[488–9]

### VOLUMETRIC

The gravimetric methods using the zinc or barium ion as precipitants have, as in orthophosphate analysis, their counterparts in volumetry. Excess of barium hydroxide may be determined by simple acidimetric titration[475]; this rapid method is to be preferred to the gravimetric barium sulphate finish. The sulphuric acid liberated when zinc pyrophosphate is precipitated with zinc sulphate may be titrated with alkali using bromophenol blue as indicator[490] or electrometrically[478]; prior adjustment to the bromophenol blue end point with acid or alkali is necessary. Better recovery figures have been obtained for pyrophosphate by titrating to pH 3·8 both before and after adding the zinc sulphate solution[479]; sodium chloride, sodium sulphate, sodium perborate and sodium silicate, common constituents of detergents, were shown not to interfere but quinhydrone must be added when peroxy compounds are present.[491] Pyrophosphate may be determined in the absence of other phosphates by the addition of barium chloride solution at pH 4 and subsequent titration with alkali of the liberated hydrion.[480] The precipitate formed is claimed to be

$$Ba_2P_2O_7.Ba_{1.5}HP_2O_7,3H_2O.$$[492]

The precipitation of heavy metal phosphates is essential at some stage in all the titrimetric methods of determining mixtures of condensed phosphates. Dworzak and Reich-Rohrwig[493] determined pyrophosphate in the presence of orthophosphate by titration with uranyl acetate solution, a permanent precipitate due to orthophosphate being produced with excess of the reagent.

The above method is long (6 hr.) and somewhat empirical; Nielsch and Giefer[494] in much later work precipitated manganese pyrophosphate at pH 4·1, dissolved the filtered precipitate in a solution of the disodium salt of EDTA and titrated the excess of manganese chloride with zinc sulphate solution. Recent papers describe methods based on the precipitation of zinc[495–6] and calcium pyrophosphates.[495]

Whilst several methods exist for estimating mixtures of condensed phosphates[497–8] good accuracy is difficult to achieve, particularly where one or more of the constituents is obtained by difference. Chromatography (q.v.) has shown that there can be twenty or more constituents in a phosphate glass so that when using older 'wet' methods on this type of sample results should be interpreted with caution. Ortho-, pyro- and meta- phosphoric acids have been estimated by Aoyama[499] by first precipitating the silver salts in neutral solution, measuring the excess of silver nitrate solution by a Volhard titration, then removing the silver with hydrogen sulphide. The free acids left are titrated to both methyl orange and phenolphthalein, with sodium hydroxide solution. This method was criticized and a modified procedure suggested,[493] but further work by Aoyama[500] verified his own method. Another procedure[501] omits the silver sulphide precipitation stage but titrates the hydrogen ion liberated when silver phosphate is precipitated. However, the indicator colour match required by this method is tedious, requiring the construction of a nomograph curve, but an allowance can be made for the presence of any strong mineral acids. Brown[502] discusses the analysis of commercial mixtures of the three acids.

The presence of linear phosphates in mixtures adds greatly to the difficulty of making an accurate analysis. Jones[503] has developed a volumetric method, based upon the precipitation of barium and manganese salts, which gives a total linear phosphate figure but unless the linear phosphate content is small compared with the pyrophosphate content the manganese pyrophosphate precipitate may not be quantitative owing to the complexing action of the linear phosphate. An extension of this method for the analysis of Graham's salt has also been described.[504] An improved method developed by Raistrick *et al.*[487] for the analysis of commercial sodium triphosphate combines volumetric and gravimetric procedures. Zinc pyrophosphate and zinc sodium triphosphate are quantitatively precipitated and the zinc content of the precipitate determined by oxine, thus enabling the amounts of the two constituents of the precipitate to be calculated. The filtrate from the zinc pyrophosphate and zinc sodium triphosphate precipitation, which contains orthophosphate and trimetaphosphate, is boiled with sulphuric acid to ensure hydrolysis and the total orthophosphate determined. Phosphate glass is estimated using benzidine and a separate total orthophosphate determination is carried out. It is suggested that the zinc precipitate is not of theoretical composition and a standard curve using pure materials be used[505]; the determination of the zinc using an EDTA titration is also preferred. Akiyama *et al.*[506] also suggest quantitative precipitation of triphosphate and pyrophosphate with zinc ion followed by an EDTA titration of the zinc triphosphate precipitate dissolved in ammonia.

A somewhat empirical method for the determination of 'sodium hexametaphosphate' is described[507] in which a precipitate formed with calcium chloride solution redissolves on the addition of more calcium chloride solution. The end point is the point at which any cloudiness has disappeared; the reactants must be kept at pH 7.

Thermometric techniques have been applied to the volumetric analysis of mixtures of ortho-, pyro- and 'meta-' phosphoric acids.[508] One advantage claimed is that neutralization may be carried out at low temperatures, so avoiding any hydrolysis.

Sodium triphosphate hydrolyzes in 1% sodium hydroxide solution in 60 hr. to give equimolar quantities of ortho- and pyro-phosphates[509]:

$$Na_5P_3O_{10} + 2NaOH \rightarrow Na_4P_2O_7 + Na_3PO_4 + H_2O$$

This reaction has been made the basis of a method using boiling 10–20% sodium hydroxide solution to raise the temperature and hence increase the speed of the reaction. The original orthophosphate is first determined, then the total phosphate, and finally the orthophosphate after hydrolysis.[510]

Acid hydrolysis is an effective method of determining the average chain length of a condensed phosphate sample. It is claimed to compare well with ion exchange methods.[511]

### SPECTROPHOTOMETRIC

Clearly, all condensed phosphates can be determined by a prior hydrolysis to orthophosphate followed by a spectrophotometric finish. This technique is used when a particular species has been isolated, for example by paper or ion exchange chromatography. It also may be used to determine total condensed phosphates in orthophosphates by solvent extraction of the orthophosphate as the molybdophosphate complex[204] and then determining the total condensed phosphates in the aqueous layer.

The complexing effect of sodium pyrophosphate and sodium triphosphate on the ferric ion has been made the basis of a method.[512] The optical density of ferric thiocyanate solution is reduced by both the compounds, but by measuring the decrease at two pH values the proportion of each is found. No large excess of either of the components should be present. The complexing effect of pyrophosphate on the 1:10 phenanthroline ferrous complex is used[513] to determine less than 1% of pyrophosphate in the presence of orthophosphate. Kolloff *et al.*[514] have determined 0·01% of pyrophosphate in orthophosphate using the ferric thiocyanate procedure. Interference may be expected from those ions which normally interfere in the thiocyanate procedure for iron. The ability of various condensed phosphates to form complexes with ferric ion has been the subject of a spectrophotometric study.[515]

### TURBIDIMETRIC

Long chain (glassy) phosphates in detergent mixtures, it is claimed, may be determined by a turbidimetric procedure. After removal of any peroxy compounds or anionic surfactants, an acetic acid solution of the sample is caused to react with *o*-tolidine and the turbidity measured at 425 mμ.[516]

### CHROMATOGRAPHIC SEPARATIONS

Chromatographic methods (paper, ion-exchange and thin-layer chromatography) have superseded nearly all 'wet' methods of condensed phosphate analysis by virtue of speed, accuracy and, particularly by using ion-exchange techniques, the ability to resolve complex mixtures.

#### *Paper*

Following earlier qualitative work[517–9] on the separation by one-dimensional paper chromatography of some of the components of a mixture of orthophosphate, pyrophosphate, triphosphate, trimetaphosphate and tetrametaphosphate, Ebel and Volmar,[520] by using two-dimensional techniques employing both an acidic and a basic solvent, separated such a mixture with the addition of hexametaphosphate. These workers showed that the cyclic and linear phosphates occupied distinct positions and within each group the $R_f$ values are a function of the molecular weight. These separations were applied quantitatively[521]; a typical basic solvent mixture for the first development contains ammonia, *iso*-propanol, *iso*-butanol and water. After drying, further separation is obtained in the second dimension with the acidic solvent, typically *iso*-propanol, water and trichloroacetic acid. The individual species are cut from the paper after being rendered visible, are wet-oxidized and the orthophosphate determined colorimetrically. The bands (from streak application) or spots, after being hydrolyzed *in situ* with acid molybdate, followed by reduction with stannous chloride or hydrogen sulphide, may be eluted sequentially from the paper and the phosphorus determined colorimetrically.[522] A third method, applied to the determination of small amounts of orthophosphate in triphosphate mixtures[523] is to leach the spot from the paper with water prior to colorimetry.

Cellulose column chromatography has been successfully applied to the separation of linear from cyclic phosphates using either acidic or basic solvents.[524]

Orthophosphates and eight condensed phosphates have been determined[525] by techniques based on methods developed by Grunze and Thilo,[526–7] who themselves used modifications of the methods of Ebel *et al.*[520] Variables affecting the separation of condensed phosphates have been studied[528] using an ascending technique, deliberate variation of solvent serving to identify higher polymers. Small amounts of the ammonium cation are necessary in solvent systems containing water, trichloroacetic acid and *iso*-propanol. This may be replaced by other bases, and the number of components separated decreases and the extent of the separation increases with increasing amounts or strength of base.[529] Breakdown of the paper with perchloric acid prior to colorimetry has been used,[530] the suggested amount of sample per spot containing 70–100 μg. of phosphorus.

The densitometer has been applied to the quantitative evaluation of the spot after spraying: ortho- and pyro-phosphate have been determined to ±2%[531] in binary mixtures, whilst results on mixtures of condensed phosphates give good agreement with elution methods.[532] It is normally considered that only unidimensional chromatograms are suitable for quantitative evaluation with this type of machine. For these the sample is applied in the form of a uniform streak across a paper strip. The concentration of component will then vary only in the direction of development and not in the direction of the streak. With streak traces, it can be seen that providing the scanning slot is narrow enough to allow discrimination of traces, and long enough to even out irregularities in the surface or in the component concentration, then its size is not critical. On the other hand for spot form traces, the aperture must be longer than the widest trace, as the concentration of component is varying in two dimensions. It can be shown that for such spot form traces reproducible calibration curves cannot be obtained. Consider such an amount of sample that will reduce the incident light falling on it by 50%, and let it be in the form of a strip of length $b$

and width $a$. Let the scanning aperture be of the same dimensions. If now the sample is concentrated into an area of length $b/2$ and width $a$, the total transmission will be 12½% due to the sample plus the 50% transmitted where there is no sample, giving a total of 62½%. Thus the smaller is the sample area the less will be the integrated counts even though the amount of sample remains constant. The preparation of reproducible calibration curves thus appears impossible, and work in the authors' laboratory has verified this.

One way out of this difficulty of calibration is to scan the spot with an aperture several times smaller than the smallest spot (the multiple scanning technique). It can be shown that this method, theoretically, gives reproducible calibration curves.

The use of mineral acids to adjust the acidity of solvents should be avoided in order to prevent hydrolysis[521] and where the separation may take several hours, as in the analysis of phosphate glasses,[533] a reduced temperature of 4°C. is recommended.[534] If this is not practicable a correction procedure may be applied.[535] To estimate the average chain length of very long chain phosphates, up to 5000, a diluted Ebel's[521] reagent is used.[536]

Specific applications of quantitative paper chromatography include the analysis of simple and condensed phosphates in water treatment plants,[537] the analysis of commercial sodium triphosphate and detergents,[535] the analysis of phosphate glasses,[538] the determination of condensed phosphates in rat urine[539] and in sausage meat,[540, 541] and the determination of less than 0·1% of pyrophosphate in orthophosphate.[542] A general review is given by Hettler.[543] A paper impregnation method is described by Kiełczewski in which sodium pyrophosphate may be determined in the presence of sodium orthophosphate. The sample solution forms a white spot on copper ferrocyanide-treated paper, the area of which increases linearly with the amount of pyrophosphate present.[544]

### *Ion-Exchange*

Beukenkamp, Rieman and Lindenbaum[545] showed both theoretically and practically that good buffering is necessary in order to separate ortho-, pyro- and triphosphate on anion exchange resins. The buffering should be in the pH range of 5·0–7·0. The ion exchange equilibria may be represented[546]:

$$\begin{aligned}
2RCl + HPO_4^{2-} &\leftrightharpoons R_2HPO_4 + 2Cl^- \\
2RCl + H_2P_2O_7^{2-} &\leftrightharpoons R_2H_2P_2O_7 + 2Cl^- \\
2RCl + H_3P_3O_{10}^{2-} &\leftrightharpoons R_2H_3P_3O_{10} + 2Cl^-
\end{aligned}$$

So that the concentration of each species leaving the column shall be approximately constant, it was suggested that three buffer solutions be used, each increasing in potassium chloride strength.[547] Ortho-, pyro-, tri-, tetrameta- and trimeta-phosphates were separated in this order with this technique, using potassium acetate/acetic acid buffer at pH 5·0 and Dowex 1 × 10 ion exchange resin. Ammonia/ammonium chloride is also an effective buffer and again using various concentrations of potassium chloride tri-, tetra-, trimeta- and tetrameta- were separated.[548] The use of gradient elution has eliminated the need for several elutant solutions. A closed mixing bottle containing 0·1 M. potassium chloride buffered at pH 5·0 is connected to a reservoir containing 1 M. potassium chloride buffered to pH 5·0. The column is fed from the mixing bottle and the concentration of the eluate at time $t$ may be calculated from the equation:

$$\log \frac{(M_1 - M_2 - M)}{M_1} - \frac{v}{2{\cdot}303\,V}$$

where $M_1$ = molarity in reservoir, $M_2$ = molarity in mixing bottle, $M$ = molarity of eluant entering the column, $V$ = volume of solution in mixing bottle and $v$ = total volume of eluate. Mixtures containing only ortho-, pyro- and tri-phosphate are best separated with water initially in the mixing bottle.[549] By using smaller resin particles (200–400 mesh size instead of the usual 100–200 mesh size) the efficiency of separation may be increased, but this requires the use of a pressure head at the column inlet for a reasonable flow rate to be maintained.[550] Complete separation of species up to heptaphosphate is claimed[551] whilst the use of anion exchange resins to separate species up to undecaphosphate is suggested.[552]

Later workers have separated the linear polymers up to tridecaphosphate and three cyclic polymers; evidence is also given that the linear polymers are eluted in the order of their increasing degree of polymerization.[553] Commercial sodium triphosphate is analyzed for ortho-, pyro-, and tri-phosphate[546] and also for trimetaphosphate[554]; in each case the fractions are hydrolyzed with sulphuric acid and the resulting orthophosphate determined colorimetrically. Sodium triphosphate has also been analyzed by a reverse flow ion exchange method, the phosphate species being fractionated on a resin column with a pressurized, continuous gradient, and then eluted by reverse eluant flow.[555] Pyrophosphate, below 0·2% by weight in orthophosphate, may be determined by eluting the orthophosphate from the column with a 0·05 M. hydrochloric acid/0·1 M. potassium chloride solution, followed by a molar potassium chloride solution to elute the pyrophosphate.[556] Pyrophosphate may also be determined in bone tissue by a similar technique.[557]

The Technicon AutoAnalyser has been applied to the determination of total phosphate in the column eluate, each species being represented as a Gaussian peak on a recorder chart, the area of which is proportional to the concentration of the species in the sample.[558]

### RADIOMETRIC

The pyrophosphate and triphosphate content of commercial sodium triphosphate may be determined by isotope dilution, since both sodium pyrophosphate and triphosphate may be prepared from the mixture in a high state of purity. A determination requires 1–3 days to complete (using 2–4 man hours) so is unlikely to compete with chromatographic methods; however, it is a useful method.[559] The technique has also been applied to the study of the tris(ethylenediamine)cobalt(III) pyrophosphate precipitate.[486] Orthophosphate containing $^{32}P$ has been used to confirm the absence of orthophosphate contamination of the pyrophosphate eluted from an anion exchange column.[557] Migrations of several condensed phosphate species labelled with $^{32}P$ have been followed both on paper chromatograms and on electrophorograms.[560] Quantitative comparisons of the different amounts of the constituents of phosphate glass, resulting from heating $Na_2HPO_4$ and $NaH_2PO_4$, both labelled with $^{32}P$, have been made by measuring the activity of each spot on the chromatogram; a sensitivity down to $10^{-9}$ g. of phosphorus is claimed.[561]

### ELECTROMETRIC

Orthophosphate may be titrated amperometrically in perchloric acid solution with bismuthyl perchlorate solution as titrant.[562] This finish has been applied to the determination of trimetaphosphate in the presence of orthophosphate, pyrophosphate, or tripolyphosphate after prior separation of the trimetaphosphate with barium perchlorate solution.[563]

Hexamminecobalt(III) chloride may be used as an amperometric titrant for determining pyrophosphate in the presence of orthophosphate.[564] The dropping mercury electrode is used as the indicator electrode, with sodium nitrate added as the supporting electrolyte. When the pyrophosphate content is small, alcohol is added to reduce the solubility of the hexamminecobalt(III) monosodium pyrophosphate, $[Co(NH_3)_6]NaP_2O_7$, precipitate. Triphosphate and hypophosphite do not give a precipitate but hypophosphate does. 'Glassy' phosphates also interfere by preventing the precipitation of the pyrophosphate. A similar method, using hexaureachromium(III) chloride, $[Cr(CON_2H_4)_6]Cl_3$, as titrant has also been used.[565–6] Sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium metaphosphate and sodium pyrophosphate have been titrated potentiometrically at 350°C. with sodium peroxide in molten potassium nitrate. An oxygen electrode is used as indicator and the Ag/Ag$^+$ electrode as reference. The average error claimed is ±2% for the mixture of the four compounds.[567]

## Reduced Phosphates

### GRAVIMETRIC

Silver hypophosphate, $Ag_4P_2O_6$, is precipitated from acid solution containing up to 0·5 M. nitric acid; to prevent any possible reduction of the silver nitrate by other reducing oxy-anions of phosphorus present, Palmer[568] has suggested the prior precipitation of zinc hypophosphate in M. sodium acetate solution. This separates hypophosphate from phosphite and hypophosphite, separation from any phosphates then being achieved by dissolution in nitric acid followed by precipitation of silver hypophosphate. The precipitate is filtered, dried and weighed.

Excess of mercuric chloride solution will quantitatively oxidize, in 3 hr., the hypophosphite ion producing a stoicheiometric amount of mercurous chloride which is filtered off, dried and weighed. This method was recommended for the assay of pharmacopœial sodium hypophosphite,[569] but Bond[570] found that the method was unsatisfactory. Hypophosphite is also claimed to precipitate silver quantitatively from silver nitrate solution containing nitric acid, and has been determined in mixtures with phosphate and glycerophosphate using this technique.[571] These indirect gravimetric methods are not, however, to be recommended, owing to the ease with which volumetric methods may be applied.

### VOLUMETRIC

Hypophosphate can be determined in mixtures of orthophosphate and phosphite by the precipitation of silver hypophosphate at pH 1–2.[572] The precipitate is filtered off and the excess of silver in the filtrate titrated with potassium thiocyanate solution by the method of Volhard. It is claimed that at pH 1–2 the reducing action of any hypophosphite is negligible.

Whilst phosphorous, hypophosphorous and hypophosphoric acids may be titrated easily with alkali – or their sodium salts titrated with acid – in mixtures, end points are difficult to distinguish, and also phosphoric acid, if present, would be titrated. Therefore redox titrations are invariably employed.

In a neutral solution of the three acids, only phosphorous acid is oxidized by an excess of iodine solution; oxidation is complete and quantitative in one hour.[573–5] Hypophosphorous acid may be determined, together with phosphorous acid, by iodine oxidation under acid conditions. Oxidation is said to be complete in 10 hours,[574] but improved methods[575–6] reduce this time to 3 hours. Excess of iodine may be determined by arsenious acid solution or sodium thiosulphate solution. A bromine/potassium bromide solution may also be used to determine phosphorous acid either by titration of the excess of the reagent[577–8] or titration of the orthophosphoric acid formed during the oxidation.[579] A combination of these two methods has been used to determine mixtures of phosphorous and hypophosphorous acids.[577] Hypophosphites used in pharmaceutical preparations have been determined using bromine oxidation methods, excess of bromine being determined by the addition of potassium iodide and titration of the liberated iodine with sodium thiosulphate solution using starch as indicator.[580–2] Whereas bromine will oxidize hypophosphite and phosphite in strongly acid solution (the kinetics of which have been discussed by Griffith and McKeown[583]), hypophosphate is quantitatively oxidized only within the range pH 6–9, the maximum oxidation rate occurring at pH 7·7.[568]

Hypophosphorous, phosphorous and hypophosphoric acids are quantitatively oxidized at the boiling point in acidified potassium permanganate solution. Hypophosphorous and phosphorous acids have been determined in this way, the excess of potassium permanganate remaining after 25 minutes oxidation being titrated with oxalic acid solution.[584] Using ammonium molybdate as catalyst Schwicker[585] found that the oxidation of hypophosphite may be accomplished at 50°C. in 30 min. In boiling neutral solution hypophosphite, whilst still oxidized quantitatively to phosphate, only reduces the permanganate to manganese dioxide, which can be filtered off prior to the determination of the excess of permanganate.[586] This method has been criticized[587] owing to the probable reduction of some of the permanganate on boiling. The reduced acids in red phosphorus have been determined by extracting the phosphorous acids with boiling hydrochloric acid, neutralizing to methyl orange and boiling this solution with potassium permanganate. Excess of potassium permanganate is determined by the addition of potassium iodide and hydrochloric acid and titration of the iodine liberated with sodium thiosulphate solution.[588] Permanganate is reduced by hypophosphites or phosphites in alkaline solution first to manganate, then to manganese dioxide. The first stage is complete after one minute at room temperature when complete conversion to phosphate occurs. The second stage is slow and it is necessary to boil the solution. Normally the excess of permanganate cannot be titrated after the first stage; otherwise the manganate would also be titrated, but if a barium salt is added then insoluble barium manganate is precipitated and the excess of permanganate may be titrated (using a formate titration) without interference.[589] Heredia[590] has confirmed this method but he prefers to back-titrate the excess permanganate using sodium oxalate solution.

Other oxidants may be used to convert the reduced phosphate to orthophosphate. Both phosphorous and hypophosphorous acids are oxidized by iodic acid in sulphuric acid solution; the iodine liberated is distilled off and absorbed in potassium iodide solution[591] or the excess potassium iodate determined.[591–2] Phosphorous and hypophosphorous acids are also oxidized in acidified, boiling (under reflux), potassium dichromate solution. Oxidation is complete in 1 hr. and the excess of potassium dichromate is determined by the addition of potassium iodide and titration of the liberated iodine.[593]

Cerium$^{IV}$ will oxidize hypophosphite to phosphite in sulphuric acid solution in 1·5 hr. at 20°C. or in 0·5 hr. at 60°C. In excess of boiling cerium(IV) both phosphite and hypophosphite are oxidized to phosphate. Bernhart[594] estimated both hypophosphite and phosphite in mixtures of the two by applying both these reactions. The addition of silver sulphate as catalyst is said to make the oxidation of both hypophosphite[595] and phosphite[596] take place more smoothly, and at steam bath temperatures.

Hypophosphite is quantitatively oxidized to phosphite by titration with ferric ammonium sulphate, the excess of which is estimated by titration with standard ceric sulphate solution [597] or sodium vanadate.[598] This reaction has been applied to the determination of hypophosphite in nickel plating electrolytes.[599] Palladium chloride is claimed to catalyze the further oxidation with ferric ion of phosphorous to phosphoric acid; the reaction is complete in ten minutes on the steam bath using 100% excess of ferric ammonium sulphate solution.[600] Both silver and manganous ions have also been used as catalysts, hypophosphite requiring 7 min., and phosphite 10 min. at 100°C. for complete oxidation.[601]

The hypophosphite content of electroless plating solutions has been determined by catalytic oxidation to phosphorous acid and hydrogen, using a catalyst prepared by successively plating silver and palladium on to a copper gauze. In the plating solution the palladium black becomes coated with nickel, so that the activity of the catalyst is then constant, and hydrogen is produced in an amount proportional to the concentration of hypophosphite. The hydrogen is burnt at a jet and the flame temperature measured using a thermocouple and recorder.[602]

### SPECTROPHOTOMETRIC

Ammonium molybdate in sulphurous acid solution forms a blue colour with hypophosphites but not phosphites.[603] The intensity of this colour is read at 470 mμ against a blank, and the percentage of hypophosphite read from a calibration curve; 470 mμ is an absorption minimum, chosen deliberately to reduce the sensitivity; measuring at 680 mμ gives much greater sensitivity. Phosphate interferes in the method but may be determined separately by the molybdovanadophosphoric acid method. Boiling ammonium molybdate solution is also reduced by the hypophosphite ion to give a blue colour; phosphate interferes but is removed by precipitation as magnesium ammonium phosphate.[598]

The reagent of Lucena-Conde and Pratt[297] contains molybdenum(VI) and molybdenum(V) in molar ratio 3 : 2, in 10 N. sulphuric acid together with 3 N. hydrochloric acid. At room temperature this reagent forms a blue colour with hypophosphoric acid with absorption maxima at 590 mμ and 670 mμ.[604] Hypophosphorous and phosphorous acids do not form a coloured complex, whilst moderate amounts of orthophosphate can be tolerated.

Sodium hypophosphite has been determined in electroless plating solutions by the decolorizing effect of the hypophosphite ion on methyl orange, the decolorization time being in inverse proportion to the amount of hypophosphite in the solution. Ferric iron and aluminium cause serious interference.[618]

## CHROMATOGRAPHIC SEPARATIONS

### *Paper*

Whilst several workers have separated mixtures of reduced phosphates by paper chromatography,[605–10] little attempt has been made to adapt the methods quantitatively; presumably once a reduced phosphate has been identified, a volumetric method applied to the original mixture is quicker and gives greater accuracy. Chromatographic separations are necessary where other oxidizable compounds are present which would interfere in the oxidimetric methods. Any of the quantitative finishes described for the paper chromatography of the condensed phosphates (*q.v.*) may be applied, provided that the reduced phosphate is first oxidized with nitric acid and bromine to convert it to phosphate.

A typical mobile phase separating phosphite, hypophosphite, hypophosphate and phosphate, on Whatman No. 4 paper, is a mixture of *iso*-propanol, *iso*-butanol, water and 20% *d* 0·880 ammonia solution in the ratio by volume 30 : 15 : 47·5 : 7·5.[606] Separation is very slow (20 hr.) and a faster separation (2–4 hr.) is achieved for the same mixture using methanol, dioxan, and N. ammonia solution in equal volumes. Using this mobile phase, and a quantitative finish based on the Lucena-Conde and Pratt reagent,[297] recoveries within 2–3% of the content of each spot are claimed.[611]

### *Ion Exchange*

Hypophosphite, phosphite and phosphate in admixture have been separated by ion exchange chromatography[612] by a gradient elution technique similar to that applied to condensed phosphates (*q.v.*) by Grande and Beukenkamp.[549] Two schemes of separation were developed. The one using potassium chloride solution buffered to a pH of 6·8 eluted the components in the order: hypophosphite, phosphate, phosphite. The other, using potassium chloride solution adjusted to a pH of 11·4 by the addition of ammonia solution, eluted the components in the order: hypophosphite, phosphate, phosphite. The effect of temperature on the separation was also studied, the retention volumes being lowered with decrease in temperature and the effect being greatest for phosphite. The scheme used at pH 6·8 has been extended to cover the separation of hypophosphite, phosphate, phosphite, hypophosphate, diphosphite (added as the sodium salt $Na_3HP_2O_5.12H_2O$), pyrophosphite ($Na_2H_2P_2O_5$), isohypophosphate ($Na_3NP_2O_6.4H_2O$), pyrophosphate,[613] and the sodium salt of the acid, designated $Na_5P_3O_8,14H_2O$. The anions were eluted in the order given, maximum separations being achieved when the amount of phosphorus per species was less than 2 mg.

A general scheme for the adaptation to the AutoAnalyser of ion exchange separations of phosphorus anions including reduced phosphates has been developed.[614]

**Refs. p. 1287**

ELECTROMETRIC

A mixture containing hypophosphorous acid, phosphorous acid and phosphoric acid can be resolved by a pH titration.[615] The quoted pK values are $H_3PO_2$, $pK = 1{\cdot}0$; $H_3PO_3$, $pK_1 = 1{\cdot}4$, $pK_2 = 6{\cdot}7$; $H_3PO_4$, $pK_1 = 2{\cdot}16$, $pK_2 = 7{\cdot}16$, $pK_3 = 12{\cdot}4$. If the amount of standard sodium hydroxide solution used to the first end point is *a* ml., to the second is *b* ml. and to the third *c* ml., then the amount of hypophosphorous acid is equivalent to $(a-b)$ ml., phosphorous acid to $(b-c)$ ml., and phosphoric acid to *c* ml. The third end point (see 'Orthophosphates: volumetric', p. 1257) can be obtained only after the addition of barium chloride solution. These authors have also used thermometric and conductimetric titrations for the analysis of the same three acids but report less accurate results.

Hypophosphorous acid has been determined by a potentiometric titration with silver nitrate solution using a silver foil indicator electrode with a saturated potassium nitrate/calomel reference electrode. The test solution was neutralized to phenolphthalein and then buffered with disodium hydrogen phosphate solution near to the end point of the titration. Orthophosphate did not interfere in the determination.[616] Grundmann and Hellmich[617] carried out a similar titration in a buffered acetate solution using a silver iodide electrode against a normalized silver electrode. Neither phosphoric nor phosphorous acid interfered in this titration.

## Elemental Phosphorus, its Compounds other than Oxyanions

### Miscellaneous

GRAVIMETRIC

Crude phosphorus is condensed from the gas leaving the electric furnace by a water spray. A sludge is the main impurity produced; this contains some yellow phosphorus, small amounts of red phosphorus, and lower oxidation products of the element. The total yellow phosphorus content of this sludge may be determined by distillation in an inert atmosphere (nitrogen or coal gas) the phosphorus being condensed in a suitable receiver.[619] Warm water is then added to the receiver and the phosphorus is collected into a bead, which, after cooling, is rapidly dried on a filter paper, transferred to a tared beaker of water, and weighed. Volatile tarry matter, soluble in phosphorus, will also be determined as phosphorus. A less hazardous method involves the conversion of the distilled phosphorus to copper phosphide.[620] After distillation, again in an inert gas, the phosphorus is passed through a glass tube containing a tight spiral of copper gauze, 10 cm. long by 1·5 cm. diameter. Over this tube is fitted an iron gauze cylinder which is heated to dull red heat. The tube is finally cooled and weighed. The water content of the sample may be determined by fitting a tared calcium chloride U-tube after the copper gauze tube; prior drying of the inert gas is then necessary.

Crude white phosphorus,[621] or white phosphorus present in a mixture with phosphoryl chloride and phosphorus trichloride,[622] may be extracted with benzene, then precipitated as cupric phosphide by shaking this solution with cupric nitrate solution. The precipitate is not weighed directly, since elemental copper may also be precipitated, but the phosphide is oxidized to orthophosphate before determination.

Tetraphenylarsonium chloride, when added to an ammoniacal solution of potassium hexafluorophosphate at 60°C., precipitates tetraphenylarsonium hexafluorophosphate. The precipitate is filtered, washed with dilute ammonia solution, dried to constant weight at 105°–115°C. and weighed as $(C_6H_5)_4AsPF_6$.[623] The results agreed with those obtained using the reagent nitron (4:5-dihydro-1:4-diphenyl-3:5-phenylimino-1:2:4-triazole), which was first proposed as a precipitant for hexafluorophosphate by Lange and Müller.[624]

VOLUMETRIC

The total phosphorus content of red or yellow phosphorus may be determined by oxidation with 1:2 nitric acid under reflux and the resulting orthophosphate (*q.v.*) determined. This reducing action of elemental phosphorus may be utilized for its determination. The ceric ion is quantitatively reduced to cerous by refluxing an excess of ceric sulphate solution in 4 N. sulphuric acid with red phosphorus. When the red phosphorus has fully dissolved the solution is cooled and the excess of oxidant back-titrated with standard ferrous ammonium sulphate solution.[625] Iodine in buffered potassium iodide solution will also react quantitatively with red phosphorus, excess of iodine being titrated with sodium thiosulphate solution. At room temperature with a phosphorus to iodine mole ratio of 1 : 4, the reaction time is 24 hr. but this reduces to 10 hr. on heating to 60°–65°C.; a phosphorus to iodine mole ratio of 1 : 3 is necessary at the higher temperature.[626] Potassium iodate,[627] potassium periodate[628] and potassium bromate[629] in sulphuric acid solution have been used as oxidants for red phosphorus. Bromine, prepared *in situ* by acidifying a bromide/bromate mixture, will quantitatively oxidize red phosphorus at 20°C. in 3–4 hr. Excess of bromine is determined by the addition of potassium iodide and titration of the iodine produced with sodium thiosulphate solution.[630] Both bromine[631] and iodine[632-3] have been used to determine phosphorus in pharmaceutical preparations. Potassium permanganate, in acid solution, oxidizes red phosphorus to orthophosphate and this reaction has been suggested[634] as a means of determining red phosphorus; the optimum phosphorus to potassium permanganate mole ratio is 1 : 1 in a solution of N. sulphuric acid. Any temperature up to 40°C. may be used.

Yellow phosphorus is extracted from a mixture of yellow and red phosphorus with benzene, carbon disulphide, or a mixture of equal volumes of carbon disulphide and carbon tetrachloride. This last solvent, though less effective, is non-inflammable and is to be preferred for routine work, After extraction with benzene, and the addition of 3 times the quantity of ethanol, the yellow phosphorus has been rapidly determined by adding an excess of iodine/potassium iodide solution, allowing to stand for 15 min., and titrating the excess of iodine with sodium thiosulphate solution.[635]

Direct titration of phosphide phosphorus is not satisfactory and phosphides are generally determined by liberating phosphine with acid. Hydrochloric acid (1 : 3) has been used for liberating phosphine from zinc phosphide rodenticide, the phosphine being absorbed in potassium permanganate solution and the orthophosphate formed being estimated volumetrically.[636] Phosphine has also been liberated by heating the phosphide in 30% sulphuric acid, and absorbing the gas in mercuric chloride solution. After filtering, the hydrochloric acid formed was titrated with sodium hydroxide solution.[637] Phosphine has been determined in air by drawing the air through a solution of mercuric chloride, forming the complex $P(HgCl)_3$. After the addition of iodine solution, which destroys the complex, excess of iodine is titrated with sodium thiosulphate solution, the amount of iodine consumed affording a measure of the phosphine content of the air.[638] The limit of this method is 1 p.p.m. of phosphine. The contaminated air has also been passed through silver nitrate solution, which precipitates silver *via* the yellow intermediate $Ag_3P,3AgNO_3$. The excess silver nitrate is titrated with potassium thiocyanate solution.[639]

### CHROMATOGRAPHIC

The katharometer has been used as a detector for phosphine. It is claimed that 0·5 p.p.m. in air may be determined on a column, 13′ by 0·25″, of 30% Apiezon *L* on 40–60 mesh firebrick. A temperature of 35°C. was used with a helium flow rate of 25 ml./min.[640] Increased sensitivity to phosphine (and to phosphorus compounds in general) is shown by the sodium detector.[651]

Phosphorus oxychloride and phosphorus trichloride have been separated and determined using a 6′ × 0·25″ column at 63°C. of 20% silicone E301 on 80–120 mesh celite.[641] A katharometer detector was used with nitrogen as carrier gas at a flow rate of 30 ml./min.

### MISCELLANEOUS METHODS

Small amounts of yellow phosphorus in red phosphorus have been estimated by placing a drop of the carbon disulphide extract on copper sulphate impregnated filter paper. The intensity of the spot obtained is compared with standards.[642] A similar method uses filter paper impregnated with silver nitrate.[643] A review including various methods of determining red and yellow phosphorus has been published.[644]

Phosphine in acetylene has been estimated by using a fixed amount of mercuric sulphate solution of known strength and passing the gas through it until the solution is exhausted, as indicated by silver nitrate paper across the exit. The time for exhaustion is proportional to the phosphine content of the acetylene.[645] An estimate of the phosphine content of air by methods suitable for routine use may be made by drawing a known volume of air through an absorption tube containing silica impregnated with a suitable reagent. Impregnants used have been silver nitrate,[646] a copper salt together with a mercury complex,[647] and a mercury salt together with auric chloride.[648] The length of stain is compared with standard stains obtained for known amounts of phosphine in air. A strip of filter paper impregnated with silver nitrate, through which a known volume of air is passed, is also a suitable and sensitive detector.[649] In the reaction of phosphine with mercuric chloride solution, $PH_3 + 3HgCl_2 \rightarrow P(HgCl)_3 + 3HCl$, the hydrochloric acid is produced quantitatively and has been used to measure the phosphine content of air.[650] A known volume of air is drawn through the solution inside a conductance cell and the change in conductivity measured; a calibration curve is prepared by adding to the cell known amounts of hydrochloric acid. Impurities in the air other than phosphine are removed by tubes of granular calcium chloride and potassium carbonate pellets.

## Organophosphorus Compounds

### VOLUMETRIC

Mixtures of dialkyl and trialkyl phosphites may be determined by the method of Bernhart and Rattenbury.[652] In an excess of alcoholic alkali solution dialkyl phosphites react with one equivalent of alkali whereas trialkyl phosphites do not react. In alcoholic acid solution trialkyl phosphites are converted to dialkyl phosphites which may then be caused to react with a known excess of alkali. The difference in the amount of alkali consumed is a measure of the trialkyl phosphite content. The reaction of dialkyl phosphites with alcoholic alkali is also an excellent method of assay; the monoalkyl phosphite content should however be estimated by a preliminary titration to pH 6·5 with alcoholic alkali and an allowance made for the alkali consumed. Reproducible, but not stoicheiometric, results have been obtained by reaction of dialkyl phosphites with iodine dissolved in pyridine. After 30 min. in the dark the excess of iodine can be titrated with sodium thiosulphate solution. It is claimed that by this method, using a calibration curve, dialkyl phosphites may be determined in the presence of other phosphorus compounds.[653]

Assay of trialkyl phosphites may be carried out by rapid titration with iodine in methanol; reaction with any dialkyl phosphites present is slow.[654] Better oxidizing agents for trialkyl phosphite determination are perbenzoic or *m*-chloroperbenzoic acid; the latter is to be preferred as it may be obtained commercially. The trialkyl phosphite is treated with a solution of *m*-chloroperbenzoic acid dissolved in benzene. Potassium iodide is then added and the iodine, released by the excess of reagent, is titrated with sodium thiosulphate solution using starch as an indicator. This reaction is also applicable to triphenyl phosphite.

Some organophosphorus halidates and pyroesters react quantitatively with peroxide, added as sodium pyrophosphate peroxide ($Na_4P_2O_7,2H_2O_2$). The reaction is carried out in an alkaline borate buffer, the excess of peroxide being titrated iodimetrically. The following compounds were determined: *iso*-propyl ethylphosphonofluoridate, di-*iso*-propyl phosphorofluoridate, tetraethyl pyrophosphate, tetra-*iso*-propyl pyrophosphate, tetra-*n*-butyl pyrophosphate, bis(ethyl methylphosphonic) anhydride, bis(*iso*-propyl methylphosphonic) anhydride, di-*iso*-propyl phosphorochloridate and *iso*-propyl methylphosphonochloridate.[655]

Organic phosphonium salts and phosphoranes may be titrated, in acetic acid solution, with perchloric acid using crystal violet as indicator. An excess of mercuric acetate should be added before titrating the phosphonium salts.[656]

Dialkyl dithiophosphates and diaryl dithiophosphates have been determined by oxidation with iodine, which reacts forming dialkyl and diaryl phosphates. The excess of iodine was determined by titration with sodium thiosulphate solution.[657] Various thiophosphoric acid ester preparations have been determined, after initial saponification, by oxidation with bromine, followed by an iodimetric finish.[658] Dialkyl hydrogen phosphorodithioates have also been determined iodimetrically after prior conversion to their nickel salts. This is claimed to overcome interference by hydrogen sulphide and thiols by precipitation of nickel sulphide and nickel mercaptide respectively.[659]

A method is described in which zirconium is extracted from a standard solution in perchloric acid by tributyl phosphate, but only in the presence of mono-or dibutyl phosphate. The zirconium remaining in the aqueous layer is determined by an EDTA titration. By reference to calibration curves the mono- or di-butyl phosphate content of the sample may be determined.[660] Shilin *et al.*[661] have determined tributyl phosphite in kerosene solution by shaking the sample with 9 N. perchloric acid and allowing the three layers to separate. Kerosene forms the top layer, tributyl phosphate acid complex the middle layer, with perchloric acid at the bottom. By reference to a calibration curve the volume of the centre layer may be related to the amount of tributyl phosphate in the sample. A mixture of phosphoric acid, mono-, di- and tributyl phosphate can be titrated directly with alkali, and the amount of each constituent determined.[90] At pH 4·5, phosphoric acid, monobutyl phosphate and dibutyl phosphate are titrated; at pH 8·5 in the presence of sodium chloride to repress hydrolysis, monobutyl phosphate and dibutyl phosphate are titrated; and finally, after the addition of calcium chloride, the third end point of phosphoric acid is effectively reached by again titrating to pH 8·5. A mixed indicator solution is used for detecting the end points. From the volumes of sodium hydroxide solution used at the various end points the amount of each constituent may be calculated, the tributyl phosphate being obtained by difference.

### SPECTROPHOTOMETRIC

1,3,5-Trinitrobenzene in alcoholic solution reacts with dialkyl phosphites forming a wine-red colour with an absorption maximum at 465 mμ.[662] This colour obeys Beer's law and, except for di-*iso*-propyl phosphite the reaction is rapid. Whilst the method is suitable for estimating the dialkyl phosphite content of trialkyl phosphites the use of purified ethanol is necessary in order to avoid high blanks and the volumetric method of Bernhart and Rattenbury is to be preferred. Similar reactions for the determination of dialkyl phosphites have been described using cacotheline[663] and 3:5-dinitrobenzoic acid.[664]

A sensitive method for the determination of tributyl phosphate is based on the extraction of 3 ml. of uranyl nitrate solution plus ammonium nitrate solution into 25 ml. of tributyl phosphate.[665] The uranium (VI) extracted was measured at 415 mμ or 280 mμ, the latter wave-length giving increased sensitivity though less reliability than the former.

Parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate) and dimethyl parathion have been estimated in technical samples and formulations by hydrolysing the ester, and measuring the ultra-violet absorption of the *p*-nitrophenol formed.[666] Measurement is made in a 50% ethanolic solution of 0·1 N. sodium hydroxide. An allowance can be made for any free *p*-nitrophenol present in the sample. At a pH of 8·5 di-*iso*-nitroso acetone forms coloured complexes with certain phosphorus-containing insecticides and chemical warfare agents.[667–8] The following compounds were determined by measuring the absorption due to this complex at 486 mμ or 580 mμ: Tabun (ethyl phosphorodimethylamidocyanidate), Sarin (*iso*-propyl methylphosphonofluoridate), DFP (di-*iso*-propyl phosphorofluoridate), TEPP (tetraethyl pyrophosphate), methyl phosphonochloridate, paraoxon (diethyl paranitrophenyl phosphate) and parathion. Acid chlorides also reacted positively to the reaction. The above compounds also catalyse the oxidation of benzidine, forming a colour the intensity of which serves as a measure of the phosphorus compound present.[669] This reaction was first proposed by Schönemann.[670] Parathion has been estimated in the infra-red by Yu-Shih Chen[671]; absorption peaks were obtained at 7·37 μ, 9·75 μ and 10·9 μ.

A sensitive method proposed for detecting and estimating nerve gases is based on their reaction with indole and sodium perborate in which the highly fluorescent indoxyl is formed.[672]

The dimethyl, diethyl, di-*iso*-propyl and diphenyl esters of dithiophosphoric acid have been determined by the direct measurement of the colour produced by their nickel salts which were prepared by shaking a benzene solution of the sample with nickel carbonate.[673]

A non-specific method for the determination of organophosphorus compounds has been developed in which the sample, dissolved in dibutyl phthalate, reacts with an ether solution of lithium aluminium hydride forming phosphine. Air is drawn through the solution and passed through silver nitrate treated paper; the colour on the paper, due to the phosphine, is measured photometrically.[674]

## CHROMATOGRAPHIC SEPARATIONS

### *Paper*

Where separation is achieved on paper chromatograms of mixtures of organophosphorus compounds, any constituent, after being rendered visible, may be determined by wet-ashing the spot, and determining the phosphorus, as suggested by Hanes and Isherwood.[675]. To obtain enough phosphorus for reasonable accuracy it may be necessary to apply the sample in the form of a streak, or to apply several spots close together.

Several workers have separated phosphoric acid, monobutyl phosphate and dibutyl phosphate. Cerrai *et al.*[676] used downward elution of a butanol–formic acid solvent, followed by a Hanes–Isherwood[675] spray reagent or bromophenol blue solution. A quicker separation (30 min.) was achieved using upward elution of *n*-butanol-acetone-water-ammonia mixture[677]; the spray used was ferric iron solution followed by sulphosalicylic acid solution as used by Wade and Morgan.[678] Alcohol–water–ammonia mixtures were used by Shvedov and Rosyanov,[679] who revealed the spots by the Hanes–Isherwood[675] reagent. Many esters of phosphorous and phosphoric acids have been separated using various mobile phases, and using where necessary stationary phases on the paper.[680] Octyl and phenyl phosphites were separated with a liquid paraffin stationary phase and methanol, nitromethane or 2-methoxyethanol nitromethane or 2-methoxyethanol as mobile phases; allyl phosphites and phosphates with polyethylene glycol 400 stationary phase and petrol/chloroform as mobile phase, and esters of phosphoric acid with *n*-propanol/2 N. ammonia as mobile phase. Alkaline potassium permanganate solution, alkaline Universal Indicator solution, and ferric thiocyanate solution were used as spray reagents. Methylphosphonic acid, methylphosphinic acid, dimethylphosphinic acid and trimethylphosphine oxide have been separated on paper, and $R_f$ values compared with a separation using paper electrophoresis.[681]

Various phosphoric esters have been identified in muscle tissue and leaf extract using the solvent system methanol/ammonia/water.[682] Acid-soluble phosphorus compounds from plant tissues have also been separated and identified.[683-4] Sugar phosphates have been separated and identified by paper chromatography[685] and electrophoresis[686]; Agarwal *et al.*[687] claim an improved separation when borate impregnated papers are used. Good separations on circular chromatograms have been obtained of phospholipids extracted from rat tissue.[688] A sensitive spray reagent for biological phosphate esters has been developed by Rorem[689]; after development the chromatogram was immersed in 0·51% alcoholic quinine sulphate solution, dried, and examined under the ultra-violet lamp; spots containing 0·007 μ-moles of phosphorus were detected. Methods of determining the phosphorus in the spots obtained from biological material have been reviewed by Delsal and Manhouri.[287] In a later paper Usher[690] wet-ashed the spots with perchloric acid, and determined the orthophosphate formed by a molybdenum-blue method due to Bartlett.[691]

Parathion and related compounds (paraoxon, methylparathion, ethyl *iso*-chlorothion, methyl *iso*-chlorothion, *O*-ethyl-*O*-*p*-nitrophenylbenzene thiophosphate, *p*-nitrophenylacetate and *p*-nitrophenol), have been separated on a silicone impregnated paper with a 1: 1: 1 chloroform/ethanol/water mixture as mobile phase.[692] Malathion and its related compounds have been analyzed by various methods, including paper chromatography, by Yu-Shih Chen.[671] Thiophosphoric insecticides have been identified, and hydrolysis products shown by simple test-tube chromatography.[693] Malathion, Parathion, Diazinon, Guthion, Systox and Trithion have been identified in kale, after an extraction procedure. A two-dimensional procedure is recommended for the best resolution.[694] Techniques for separation of 11 insecticides have been described by Mitchell.[695] Phosphoric, phosphonic and phosphinic acid esters have been converted to acetylcholinesterase inhibitors by exposure to ketene vapour. By spraying with the enzyme (in horse serum), followed by acetylcholine chloride and bromothymol blue indicator solution, blue spots are obtained on a yellow background.[696] Acetylcholinesterase inhibition has also been applied to the detection of pesticide residues in plant tissue.[697] The method of spot detection by radioactive labelling has been applied to the detection of phosphate esters by Boursnell[698] and Winteringham.[699]

### *Thin Layer*

Esters of phosphoric acid have been separated on silica gel coated plates, and rendered visible by spraying with acid ammonium molybdate, followed by drying and exposure to ultra-violet light. Twenty-six esters were separated (using eight different mobile phases); these included trialkyl phosphates, trialkyl phosphites, amidophosphoric esters and thionophosphoric esters.[700] Alumina and silica gel have been used to separate esters and amides of various thiophosphoric acids; hexane/acetone mixtures were used as the mobile phase with potassium permanganate solution as the spray reagent.[701]

Bäumler and Rippstein[702] have separated thiophosphate pesticides on silica gel plates with hexane/acetone (4 : 1) as the mobile phase. The spots were detected using palladium chloride in hydrochloric acid. Conditions for the separation of 27 phosphorus-containing pesticides have been defined by Walker and Beroza[703]; three reagents were used for revealing the spots: iodine vapour, bromine vapour/fluorescein, and silver nitrate solution. Braithwaite[704] has shown that 0·1 μg. of certain thiophosphate pesticides may be detected on silica gel layers with 2 : 6-dichloro-*p*-benzoquinone-4-chloroimine. Good sensitivity (0·1 μg.) has been achieved using a cholinesterase inhibition technique for spot detection; 17 pesticides were detected on both silica gel and alumina.[705]

### *Vapour Phase*

The butyl esters of phosphoric acid can be converted to the volatile methyl esters by reaction with diazomethane in ether. Separation is then achieved on a 3-foot column of silicone DC 200 on firebrick at 188°C., or silicone E301 on a celite support at 197°C. This method was applied to samples of tributyl phosphate.[706] Dimethyl phosphite and diethyl phosphite have been separated using dibutyl phthalate or Apiezon K on Fluopack 80. Helium was used as a carrier gas at a temperature of 107°C.[707]

A general method has been proposed for the extraction and subsequent separation of organophosphorus pesticides in sub-microgram amounts in plant tissue, using an electron-capture ionization detector.[708] The highest sensitivity was obtained using a detector designed by de Faubert Maunder *et al.*[709] The sodium wire detector in comparison with the flame ionization detector will also give an increased response to organophosphorus compounds.[651]

The organic radical in certain organic phosphates was identified by pyrolyzing the sample and identifying the pyrolysis products by infra-red spectrophotometry or mass spectrometry after separation on the chromatograph.[710]

### ELECTROMETRIC

Trimethylphosphine oxide, tetra-*n*-octylphosphine oxide and triphenylphosphine oxide have been titrated in acetic anhydride with perchloric acid dissolved in dioxan.[771] Sharp inflexion points were obtained using a modified[712] calomel and a glass electrode.

An oscillometric method has been used to determine tributyl phosphate in kerosene solution. Oscillometric readings, which measure the change in the dielectric constant, were taken of the filtered tributyl phosphate solution after extraction of the uranyl nitrate residues with sodium carbonate solution. A calibration curve was prepared in a similar manner.[713]

Dialkyl and diaryl phosphites, either alone or in mixtures with the corresponding trialkyl or triaryl phosphite, react with carbon tetrachloride and diethylamine forming the amine hydrochloride. This reaction has been applied quantitatively,[714] the hydrochloride being titrated with sodium methoxide in methanol/benzene/pyridine solution, the end point being detected with a high frequency titrimeter.

Cathode-ray polarography has been applied to the determination of pesticide residues after separation into individual components by paper chromatography.[715-6] This technique also offers some specificity.

## Direct (Instrumental) Methods of Determining Phosphorus

Since the general application to phosphorus chemistry of spectroscopy in its many forms, has been dealt with in some detail in Section XXXIV (page 1129), it is proposed to high-light only a few specific quantitative applications here.

Of these applications mention should be made of the use of arc and spark source photographic and direct reading spectrographs in the determination of phosphorus in ferrous[717-42] and non-ferrous[743-46] metals, titanium dioxide,[747] plants,[748-9] soils[750] and phosphating baths.[751] Some work has been done on the development of nebutizers for solution analysis[752] and on sources.[753-54] Detection limits for phosphorus around 20–30 p.p.m. have been claimed.[752-4] Work in the authors' laboratory using an H.F. plasma torch as a source in solution analysis has pushed the detection limit down to 4 p.p.m. The atomic line 2535 A. was used in this work with a power of 4·9 kw. in the plasma.[755] It may be of interest to mention a solution technique based on the extraction, with butyl alcohol, of phosphorus as molybdophosphate. The extract is absorbed on powdered graphite and examined spectrographically.[756]

Flame photometric methods for determining phosphorus have been described; these employ direct emission from inorganic and organic phosphorus compounds in various solvents[757-8] or the depressive effect of phosphorus upon the emission of strontium.[759]

The *X*-ray fluorescence spectrometer has been used for the determination of phosphorus in minerals[760-2]; *X*-ray absorption methods have also been used.[763]

Radioactive phosphorus has been used to monitor the phosphorus content of molten steel in steel-making processes; the final measurement is carried out with Geiger-Müller tubes and associated equipment.[764-5]

An interesting application of nuclear magnetic resonance is that of Guffy and Miller,[766] who applied the method to the analysis of polyphosphoric acids. Finally, mention might be made of the infra-red analysis of tripolyphosphate by Suzuki *et al.*[767]

## BREAKDOWN PROCEDURES

### Inorganic

In general phosphate rocks are not completely soluble in acid although with some rocks the degree of breakdown is sufficient for many purposes; in nearly all cases an insoluble residue is left which may contain phosphorus. Rocks from the Moroccan and Florida deposits may be effectively decomposed by fusion with sodium carbonate. However, others such as those from the Senegal deposits will require fusion with sodium peroxide which in the authors' opinion is the most generally acceptable method of decomposition for phosphate rocks. Alkali hydroxide fusions may also be used but losses of phosphorus will occur if pyrosulphate fusions are attempted.[768] Acid breakdown by nitric and hydrofluoric, or nitric, hydrofluoric and perchloric acids, is also used but the presence of fluorine in the resulting solution may lead to complications in later stages of the analysis. Care should be taken both in fusions and digestions that any residue remaining is not discarded, otherwise losses of phosphorus may occur.

Alkali and alkaline-earth phosphides should be decomposed with extreme caution; violent reaction may occur with certain oxidizing agents, but cold concentrated sulphuric acid has been used to decompose sodium phosphide.[769] The authors of this Section have also decomposed calcium and magnesium aluminium phosphides with cold concentrated sulphuric acid. Metallurgical samples, where the phosphorus is present as phosphide, must be decomposed under strongly oxidizing conditions, in order to prevent loss of phosphorus as phosphine. Acid breakdown with various combinations of nitric acid, hydrofluoric acid and perchloric acid, or fusion with sodium peroxide, is generally employed.

Where the total phosphorus content of condensed phosphates, or of the individual species after, for example, ion exchange separation, is required, conversion to orthophosphate is easily effected by hydrolysis in hot strong acids.[770] Reduced phosphates may be oxidized by nitric acid and bromine water.

Inorganic phosphorus compounds that are difficult to hydrolyze, for example the phosphonitrilic chlorides, may be treated in the same manner as organophosphorus compounds and decomposed in the sodium peroxide bomb. The halides and oxyhalides of phosphorus are simply carefully hydrolyzed; where phosphorous acid results this should then be oxidized to orthophosphate.[771]

### Organic

Wet digestion procedures are greatly favoured for the breakdown of organophosphorus compounds. A variety of acid mixtures has been tried. Sulphuric acid and nitric acid mixtures have been used for microchemical breakdowns both with[85, 772–3] and without[346, 774] the final addition of hydrogen peroxide to clear the solution. Sulphuric acid and hydrogen peroxide have been used[775, 244] and this combination was found to be particularly effective for decomposing organophosphine compounds,[244] considered difficult to decompose. A mixture of sulphuric acid and potassium persulphate also effectively decomposed triphenyl phosphine.[776]

Two acid breakdown procedures have been suggested by Simmons and Robertson[777]: alkyl phosphates were completely decomposed by refluxing with hydriodic acid, and both alkyl and aryl phosphates decomposed in a mixture of nitric, sulphuric and perchloric acids with sodium molybdate added as catalyst. Selenium has also been used as an effective catalyst.[778] Alkyl and aryl phosphates also decomposed with nitric acid and, when partial breakdown had occurred, with perchloric acid.[779] The so-called liquid-fire reaction of Smith[780–1] using perchloric acid/nitric acid mixtures has been used to decompose high-explosive compounds containing phosphorus.[782] A semi-micro procedure using a mixed sulphuric perchloric acid reagent has been described by Saliman.[261] This author also used, for micro amounts of phosphorus, a digestion mixture consisting of hydriodic acid, calcium iodide, water, phenol and acetic acid; it was found particularly effective for phosphate insecticides. Kirsten and Carlsson[212] found wet oxidation methods both fast and simple.

Decomposition of biological material may be accomplished with sulphuric acid heated in a sealed tube; the method developed for nitrogen[783] was applied to phosphorus determination.[784] The Carius method of breakdown, using nitric acid in a sealed tube, can yield low results with phosphate compounds owing to attack on the glass tube; the addition of potassium chloride prevents this and good recoveries are obtained.[785] The wet oxidation and ignition of soil have been studied in order to prevent losses of phosphorus; 500°C. is suggested as an optimum temperature.[786]

Fusion methods are favoured by many workers. For microchemical determinations sodium carbonate and sodium nitrate mixture in a platinum boat has been used,[772] as has sodium hydroxide and potassium nitrate,[787] potassium hydroxide and potassium nitrate,[788] and sodium carbonate.[453] Fusions with potassium manganite[789] and sodium[790] have also been suggested.

Sodium peroxide fusion in a nickel bomb is a generally applicable method of breakdown, giving good results for triphenylphosphine.[267] The usual fusion mixture for the semi-micro bomb consists of sodium peroxide, potassium nitrate and sucrose,[267, 791–3] but a mixture of sodium peroxide and ethylene glycol has been used.[794–5] The macro bomb, using sodium peroxide and sucrose for the fusion, is also an efficient method of breakdown.[796–7] Fluorinated organic materials containing phosphorus have been decomposed in the micro bomb using semi-micro amounts of sample.[80]

Rapid micro and semi-micro determinations have been accomplished[191] by applying the Schöniger flask technique[798–9] to organophosphorus compounds, but Kirsten and Carlsson[212] found a tendency towards low results as have the authors of this Section.

## QUALITATIVE

### *Orthophosphate*

Many of the quantitative procedures which have been described are equally applicable to the qualitative detection of orthophosphate. Thus ammonium molybdate is one of the most commonly used reagents for the detection of orthophosphates.[800–3] The bright yellow precipitate of ammonium molybdophosphate can be characterized under the microscope.[804–5] Due regard must of course be taken of the previously mentioned elements that also give a precipitate with ammonium molybdate.

Magnesia mixture will give a white precipitate of magnesium ammonium phosphate with orthophosphate solutions; this again can be identified under the microscope.[804, 806]

As little as 1 microgram of pentavalent phosphorus is said to be detected in a solution containing 1 part in 50,000 as a result of the formation of quinoline molybdophosphate on a circular paper impregnated with a solution of quinoline molybdate.[807–9] *o*-Dianisidine molybdate has also been used for the detection of phosphate.[810, 811]

The various colorimetric systems for the quantitative estimation of orthophosphate are eminently suitable for its detection. Amongst these may be mentioned the various 'moly-blue' methods, both with and without extraction, the molybdovanadophosphate method and the benzidine blue methods.[800, 812–7] It may also be noted that a mixture of acid sodium molybdate solution and ferrous sulphate solution, which is colourless, becomes coloured blue upon the addition of orthophosphate solution followed by alkaline fluoride solution.[818]

### Condensed Phosphates

Whilst the most important procedures for the identification of condensed phosphates are undoubtedly those involving chromatography, some of the older methods may be of interest and these will be mentioned.

Pyrophosphoric acid may be detected in the presence of orthophosphoric acid by the characteristic appearance of copper pyrophosphate crystals when copper sulphate solution is added to the mixture.[819-21] Silver pyrophosphate, white, is less soluble than silver phosphate, yellow, in acetic acid solution; this property combined with the colour difference, has been used as a test for pyrophosphate.[819,822] The insolubility of barium pyrophosphate precipitate in acetic acid has also been used to distinguish orthophosphate from pyrophosphate.[823] Zinc pyrophosphate crystals have been examined microscopically by Heinerth.[824] The qualitative behaviour of sodium triphosphate, sodium trimetaphosphate and sodium hexametaphosphate towards sixteen metal ions has been examined.[825]

Hexamminocobalt(III) chloride gives characteristic crystals with pyrophosphate,[826] which have been examined microscopically.[821,827] This reagent has also been used for the identification of unknown condensed phosphates by examination of the crystals obtained.[828]

Highly condensed phosphates, in the presence of orthophosphate, pyrophosphate and triphosphate may be detected down to a limit of 1 part in 20,000 with cinchonine.[829] Various basic organic compounds have been used[488,830] to characterize both poly- and meta-phosphates.

Clearly, the quantitative paper chromatographic methods may also be used qualitatively, either by reference to known $R_f$ values or simple comparison with standards treated under the same conditions as those of the test. Most of the qualitative separations were described before quantitative paper chromatography became established: the separation of phosphate from arsenate, hypophosphite and pyrophosphate,[605] and the separation and identification of various condensed phosphates in synthetic mixtures[831-3] and in mayonnaise and vegetable thickening agents[834] have been described. Paper electrophoresis has been applied to the separation of condensed phosphates[835] and a general review of electrochromatographic methods has been given by Sato.[836] Singh[837] found that, of fifty-eight organic dyes tested for the detection of condensed phosphates on paper, *o*-toluidine blue was to be preferred.

Thin-layer chromatography in general gives a much faster separation than paper chromatography but does not lend itself so easily to quantitative applications. The technique has been applied qualitatively to the separation of orthophosphate and pyrophosphate[838] and, following on his earlier work on paper chromatography,[839] Roessel[840] has separated both linear (up to $n=8$) and cyclic phosphates using cellulose powder with added corn starch as binder.

## Reduced Phosphates

Hypophosphite may be distinguished from phosphite by its reaction with copper sulphate solution with which it gives, on warming, a red precipitate of cuprous hydride,[841-2] phosphite giving a light blue precipitate of cupric phosphite. Hypophosphates do not reduce copper sulphate.

Under strongly acid conditions phosphites and hypophosphites react very slowly with sodium selenite, whereas hypophosphates precipitate red elementary selenium.[843]

Whereas both phosphites and hypophosphites reduce silver nitrate solution to metallic silver,[844] hypophosphates precipitate silver hypophosphate which is not reduced even on heating.

Barium chloride solution with phosphites and hypophosphates gives white barium salts; the barium phosphite precipitate is soluble in dilute acids whereas the barium hypophosphate precipitate is difficultly soluble. Hypophosphites do not give a precipitate with barium chloride solution.[823,845]

Lead phosphite is insoluble in neutral solution and is precipitated when lead acetate solution is added to a mixture of phosphite and hypophosphite. This has been used as a method of separating hypophosphite from phosphite and phosphate.[846]

Two further methods have been mentioned by Gutbier[847] to distinguish hypophosphite from phosphite: on reaction with concentrated alkali hydrogen is released from hypophosphites, not from phosphites, and on warming with concentrated sulphuric acid only hypophosphite will liberate free sulphur.

Microscopic examination of various metal precipitates has been used for qualitative recognition of hypophosphites, *viz.* with mercurous nitrate,[848] thallous acetate,[804] lead acetate,[804] silver nitrate.[804] Phosphite precipitates have also been examined microscopically; suitable precipitants are calcium acetate and barium acetate.[805]

The reaction with iodine solution may also be used to distinguish phosphites from hypophosphites, phosphites being oxidized in neutral solution whilst hypophosphites require strongly acidic conditions.[844, 849] Acidified potassium permanganate solution has no action in the cold on phosphites, but is decolorized on warming; hypophosphites reduce it in the cold.[845] Potassium permanganate solution has also been used to detect the presence of lower oxides in phosphorus pentoxide.[850]

## Elemental Phosphorus, Its Compounds Other than Oxyanions

### Miscellaneous

The early Dusart–Blondlot method for detecting phosphorus in biological materials involves its reduction to phosphine with zinc and sulphuric acid. The phosphine, in a stream of hydrogen, is burnt at a jet, where it imparts a green coloration to the flame. It can be caused to react with silver nitrate solution and the phosphine in the precipitate regenerated with more zinc and sulphuric acid. The latter variant overcomes interference from the organic material. Modifications of the method have been proposed by Křepelka and Chmelař,[851] and Lieb and Soltys.[852] Yellow phosphorus and phosphides may be detected by passing air through the specimen contained in a sulphuric acid solution at 100°C. and passing the vapour through silver nitrate impregnated paper, when a brownish-black spot is formed. The result is confirmed by testing for phosphate after oxidation of the silver phosphide to phosphate.[853–5] A microchemical procedure for yellow phosphorus estimation based on steam distillation has been described: less than 10 $\mu$g of phosphorus is claimed to be detected.[856] Both phosphorus and phosphine have been semiquantitatively determined by measuring the amount of precipitate formed in a capillary tube immersed in ammoniacal silver nitrate solution.[857]

Following the work of Schenk and Scharff on the detection of phosphorus using the gold-leaf electroscope, Treadwell and Beeli[858] have determined phosphorus in ethylene dibromide solution and in mixtures with tetraphosphorus trisulphide.

The luminescence of yellow phosphorus, detectable in the dark, has fallen into disuse as a qualitative method, but may be used to estimate the element in the presence of phosphorus–sulphur compounds. The sample is mixed with zinc oxide and an inert solvent, then heated in the dark, the temperature at which luminescent vapours are observed being recorded. Concentrations of 0·02–0·03% of yellow phosphorus may be detected.[859]

Phosphorus in organic compounds may be detected by fusing the sample with magnesium powder, and hydrolyzing the magnesium phosphide formed. The green flame of the phosphine is characteristic.[860]

The phosphine resulting from heating pharmaceutical preparations containing calcium hypophosphite has been detected by reaction with sodium aurichloride on filter paper; a violet coloration is obtained.[861] Silver diethyldithiocarbamate gives a colour reaction with phosphine, the absorption maximum differing from that of arsine and stibine, and has been used by Vašák[862] for its detection. This author also proposed the silver salt of 2-mercaptobenzimidazole for the detection of phosphine, white phosphorus and lower oxidation products of phosphorus.

Chemical microscopy has been applied to the identification of the phosphoramidic, phosphorodiamidic, triphosphenimidic and tetraphosphenimidic acids by examination of their *o*-tolidine, ammonium and silver salts.[863]

2-Chloro-1 : 3 : 5-trinitrobenzene (picryl chloride) in acetone reacts with filter paper impregnated with alkaline hydrazine sulphate solution, forming a pink colour. This reaction has been used to detect phosphorus pentachloride in the presence of phosphorus trichloride; the sample is heated with picric acid forming, in the case of phosphorus pentachloride, picryl chloride, which is then used in the test. Phosphorus trichloride does not form picryl chloride.[864]

The ions phosphate, difluophosphate and monofluophosphate may be detected in mixtures by paper electrophoresis at pH 7, which gives a spot for phosphate and one for mono and difluophosphate.[865]

Using a solvent containing *iso*-propanol, water, trichloroacetic acid and ammonia, Steger and Seener[866] have separated the phosphate, monothiophosphate, dithiophosphate, monothiophosphite, monothiohypophosphite and dithiohypophosphite ions by paper chromatography; dithiophosphate which hydrolyzes at ordinary temperatures was found to give an $R_f$ value at 4°C.

## Organophosphorus Compounds

Some colour reactions of organophosphorus compounds have been studied by Hecker and Hein.[867] Phosphine oxides and dialkylphosphinic acids give a deep blue colour when heated with anhydrous nickel bromide in toluene. Alkyl phosphine oxides and tetra-alkylphosphonium salts form a deep violet colour with *m*-dinitrobenzene in sodium hydroxide solution. Tertiary phosphines react with 3 : 5-dinitrobenzoic acid to give a red-violet colour, alkylphosphine sulphides give a blue colour when heated with vanillin and hydrochloric acid, and alkylphosphine oxides give a brown or green colour when heated with carbon disulphide, sodium hydroxide and a molybdate.

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## SECTION XXXVI

# THE RADIOCHEMISTRY OF PHOSPHORUS AND ITS COMPOUNDS

### BY N. R. LARGE

## TABLE OF PHOSPHORUS ISOTOPES

THE following Table presents a complete list of all the radioactive and stable isotopes of phosphorus, together with a number of their salient features, as recorded in the literature or by private communication by approximately February, 1958. It has been prepared directly from the *Table of Isotopes*, by Strominger, Hollander, and Seaborg[1] with the kind permission of the authors. This introduction is based on that to the original Table.

A description of the entries in the various columns is given below.

### ISOTOPE

The first column contains the atomic numbers, chemical symbols, and mass numbers of the nuclear species. The stable isotope is underlined.

### HALF-LIFE

All half-life values have been determined by direct measurement of decay rate. An attempt has been made to list the most precise value or values first.

### TYPE OF DECAY

Since many classes of data are included in the third column, the entry denoting mode of decay is preceded by the special symbol for radiation, ⊙. Symbols used are

| | |
|---|---|
| $\beta^-$ | Negative beta-particle (negatron) emission. |
| $\beta^+$ | Positive beta-particle (positron) emission. |
| $\alpha$ | Alpha-particle emission. |

When experimenters have searched for and failed to find a particular mode of decay, this is indicated, for example, as 'no $\beta^+$'. Experimental upper limits are given, and are indicated by 'lim', but no theoretically predicted limits have been quoted.

### CLASS AND IDENTIFICATION

The degree of certainty of each isotopic assignment is indicated by a letter in the third column according to the following code:

| | |
|---|---|
| A | Element and mass number certain. |
| B | Element certain and mass number probable. |

Data which have been shown to be in error have not, in general, been included in the Table.

The means by which the mass assignments were made are next tabulated. In general, several references are given here, the first of which denotes the probable discoverer of the isotope. Following this, references are given to the papers which contributed most significantly toward giving the isotope its best or present rating. Some indication of the experimental methods used in making the various assignments may be had from the following symbolism:

| | |
|---|---|
| chem | Chemical separations, establishing uniquely the chemical identity (atomic number) of the isotope. |
| genet energy levels | Proof of isobaric relationship with an identified nuclide by observation of identical energy levels following decay of both, implying decay to the same product. |
| excit | Loosely refers to energetic considerations which have aided in making the mass assignment. Some of these might be<br>(1) excitation or yield experiments to establish the nuclear reaction which produces the isotope,<br>(2) bombardments with low energy particles, in which possible products are few,<br>(3) mass calculations, or other estimates or measurements of $Q$ values. |
| cross bomb | Studies of yields of the isotope in several different types of bombardments, in which the target elements as well as the projectiles have been varied. |
| *n*-capt | Cases where bombardments with slow neutrons ($n-\gamma$ reactions) have provided key evidence in the mass assignments. |
| decay charac | Identification of expected or predicted decay characteristics. |

Data on genetic relationships which have been demonstrated experimentally are located in column three underneath the class-assignment information.

### NUCLEAR MOMENTS

Measured values of the nuclear moments are also given in the third column. Unless otherwise stated, the measured value is that of the ground state. The mechanical or spin moment, I, is given in units of ħ. The magnetic dipole moment, $\mu$, is given in units of nuclear magnetons. The value is given without the diamagnetic correction.[2] In selecting these data much use was made of the compilations of Mack,[3] Walchi,[2] and Kopfermann.[4]

Experimental methods are described as follows:

| | |
|---|---|
| atomic spect | Hyperfine structure from optical spectroscopy (includes both line and band spectra). |
| nucl induct | Nuclear resonance absorption or induction. |

### ENERGY OF RADIATION

The energies of particles and photons are included together in column four. The symbol '⊙' always denotes absolute percentages of total decay. The particle energies are followed by other relevant information pertaining to the decay scheme and by a description of the experimental methods used in obtaining the data. Beta-particle energies correspond to the upper limits of the spectra, except where indicated as E (average).

Experimental methods for the measurement of the properties of particles and gamma rays are described as follows:

| | |
|---|---|
| abs | The upper limit of the $\beta$-ray spectrum is estimated from the range of the most energetic $\beta$-particles in an absorber. |
| spect | The $\beta$-particle energies are determined by magnetic deflection (magnetic spectrograph or spectrometer or counter with magnetic field). |
| scint spect | The $\beta$-particle or $\gamma$-ray energies are determined by measurement of pulses produced by a scintillating crystal or solution. |
| ion ch | The average $\beta$ energy is determined by measurement of the ionization produced in an ionization chamber by a sample whose absolute disintegration rate is known. |

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| | |
|---|---|
| calorimeter | The average $\beta$ energy is determined by measurement of the heat produced in a calorimeter by a sample whose absolute disintegration rate is known. |
| cl ch | The $\beta$-particle energies are determined by the use of a cloud chamber with a magnetic field. |

Gamma transitions are described by the following information:

### ENERGY OF THE NUCLEAR TRANSITION

This corresponds to the difference between the energy contents of the initial and final nuclear states and is equal to the photon or gamma-ray energy (if a photon is emitted in the transition).

### ABUNDANCE OF GAMMA RAYS

Intensities given with the percent sign refer to the number of unconverted photons emitted per 100 disintegrations. When attempts to find gamma radiation have failed, this is indicated by 'no $\gamma$'. Experimental upper limits are indicated by 'lim'. *X*-Rays are not mentioned.

### DISINTEGRATION ENERGY AND SCHEME

The disintegration energy, or $Q$ value, of a nuclear transformation is defined as the mass difference (expressed in Mev.) between the initial and final systems under consideration. For radioactive decay processes, $Q$ is equal to the sum of the particle kinetic energy, nuclear recoil energy, and the energies of any gamma transitions necessary to de-excite the final nucleus to its ground state. In $\beta^+$ decay the $Q$ value is given as $Q_{\mathrm{EC}}$, to avoid ambiguity associated with the addition of $2m_0c^2$ to the positron energy. Where $Q$ values have been estimated or calculated by the authors of the compilation[1] from which this Table is adapted, the special reference 'SHS' is used; otherwise, reference is made to the paper from which the quoted value is taken. In all instances $Q$ values have been obtained from decay data.

Energy-level diagrams have been drawn for all radioactive iostopes; these are not necessarily complete representations of the data, but include only those features which seem to be reasonably well established and unambiguous. Heights of the various energy levels above the ground state are indicated at the side of the drawing. Occasionally the energy value of a level is inferred from nuclear reaction data not given in the table. When the authors have altered a decay scheme in any significant way from that given in the original paper or papers, they include their own code reference (SHS).

In many cases, the total angular momentum (spin) and parity of the states are given in the level schemes. When the spin of a state has been measured directly, it is denoted by underlining that quantum number in the decay scheme, i.e. $\underline{\tfrac{1}{2}}+$. If the spin is determined uniquely by other methods, it is designated by the quantum number without any other modification, i.e. $3-$. The $0+$ character of the ground states of even-even nuclei is in this latter category except in a few cases where direct measurements of the spin have been made. Probable spin values are indicated with parentheses around the quantum number, i.e. $(2+)$. Since parity assignments depend heavily upon theory, the foregoing nomenclature does not apply to them.

The percentage figures given in the decay drawings total 100% for the total decay. In some cases the symbol † is used to designate the relative branching of one mode of decay.

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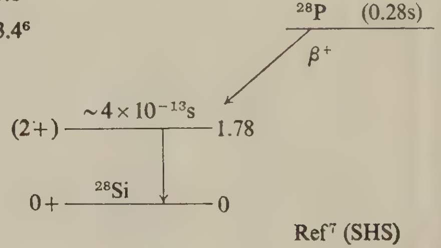
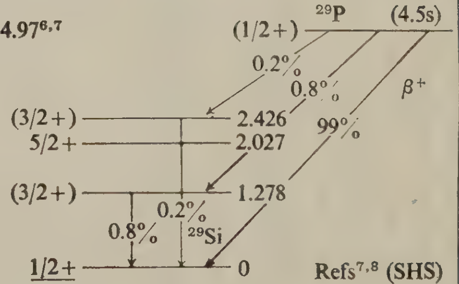
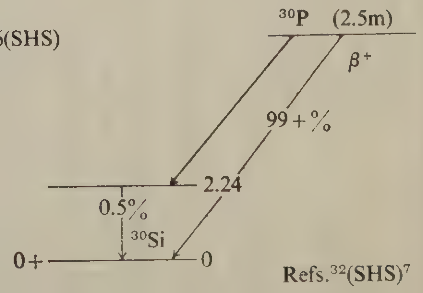
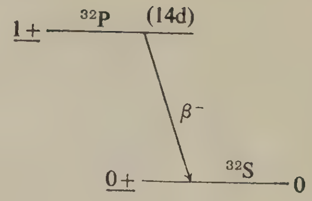
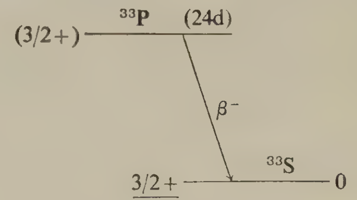
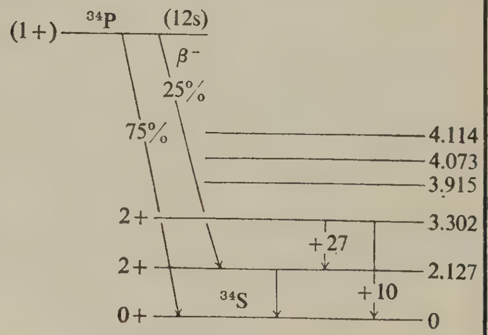
| Isotope<br>A<br>Z | Half-life | Type of decay (•); class; genetic relationships; % abundance; nuclear moments (spin 1, magnetic μ, quadrupole q) | | Energy of radiation in Mev. | | Disintegration energy and scheme |
|---|---|---|---|---|---|---|
| $^{28}_{15}$P | 0·28 s[1] | (•) | $\beta^+$, no α[1,4,2] | $\beta^+$ | 10·6 (~50%), others (~50%) scint spect[1] | $Q_{EC}$ 13.8[5]<br>$Q_{EC}$ 13.4[6]<br> $^{28}$P (0.28s)<br>$\beta^+$<br>~4×10$^{-13}$s<br>(2+)<br>1.78<br>$^{28}$Si<br>0+<br>0 |
| | 0·29 s[2] | B | excit, decay charac[4,2] | γ | 1·79 (75%), 2·6 (?), 4·44 (10%), 4·93 (?), 6·1, 6·7, 7·0, 7·6 (5%) scint spect[1] | |
| | 0·27 s[3] | | | | 1·78, 2·67, 3·01 (?), 4·3 (?), 4·6, 4·89, 5·2 (?), 5·5 (?), 6·7, 7·1, 7·4 (?), 7·7 (?), 8·1 (?) scint spect[2] | Ref[7] (SHS) |
| $^{29}$P | 4·45 s[8,9] | (•) | $\beta^+$[10] | $\beta^+$ | 3·95 spect[8,13,9] | $Q_{EC}$ 4.97[6,7]<br> $^{29}$P (4.5s)<br>(1/2+)<br>0.2%<br>0.8%<br>$\beta^+$<br>99%<br>(3/2+)<br>2.426<br>5/2+<br>2.027<br>(3/2+)<br>1.278<br>0.2%<br>0.8%<br>$^{29}$Si<br>1/2+<br>0 |
| | 4·6 s[10] | A | excit[10] | | 3·9 scint spect[12] | |
| | | | genet energy levels[8] | | 3·6 cl ch[10] | |
| | | | others[11,12] | γ | 1·28 (0·8%), 2·43 (~0·2%), no 2·03 (lim 0·2%) scint spect[8] | Refs[7,8] (SHS) |
| $^{30}$P | 2·55 m[14,15] | (•) | $\beta^+$[18] | $\beta^+$ | 3·24 spect[27,28] | |
| | 2·52 m[16] | A | excit[18,19] | | 3·23 abs[15] | |
| | 2·18 m[17] | | others[20,21,22,23,11,24,25,26] | | others[29,30,19,31] | $Q_{EC}$ 4.26(SHS)<br> $^{30}$P (2.5m)<br>$\beta^+$<br>99+%<br>2.24<br>0.5%<br>$^{30}$Si<br>0+<br>0 |
| | | | | γ | 2·16 (0·5%) scint spect[32] | |
| | | | | | no γ[27,15,33] | |
| $^{31}$P | | (•) | 100[34,35] | | | Refs.[32](SHS)[7] |
| | | 1 | ½ atomic spect[36] | | | |
| | | μ | +1·1305 nucl induct, atomic spect[37,38,39,36] | | | |

| Isotope A Z | Half-life | Type of decay ('•'); class; genetic relationships; % abundance; nuclear moments (spin 1, magnetic $\mu$, quadrupole q) | | Energy of radiation in Mev. | | Disintegration energy and scheme |
|---|---|---|---|---|---|---|
| $^{32}$P | 14·22 d$^{40}$ | ('•') | $\beta^{-47}$ | $\beta^-$ | 1·707 spect (average of 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75) | $Q_\beta - 1.704^5$<br><br>Ref.$^7$(SHS) |
| | 14·30 d$^{41,42}$ | | no $\beta^+$ (lim $1{\cdot}3\times10^{-7}$%)$^{48}$ | | E (average) 0·70 ion ch$^{76,77}$ | |
| | 14·35 d$^{43}$ | | others$^{49,50,51,52}$ | | E (average) 0·69 calorimeter$^{78}$ | |
| | 14·50 d$^{44}$ | A | chem, *n*-capt$^{53}$ | | internal bremsstrahlung$^{86,87,88,89}$ | |
| | 14·07 d$^{45}$ | | daughter of $^{32}$Si$^{54,55}$ | $\gamma$ | no $\gamma^{90,69,91}$ | |
| | 14·60 d$^{46}$ | | others$^{56,57,58,25,26,59,60,61}$ | | | |
| | | 1 | 1 nucl induct$^{62}$ | | | |
| | | $\mu$ | −0·2523 nucl induct$^{62}$ | | | |
| $^{33}$P | 24·4 d$^{92}$ | ('•') | $\beta^{-65,63}$ | $\beta^-$ | 0·249 spect$^{92}$ | $Q_\beta - 0.749$ (SHS)<br><br>Ref.$^7$ (SHS) |
| | 24·8 d$^{65}$ | A | chem, cross bomb$^{63}$ | | 0·251 spect$^{95}$ | |
| | 25 d$^{93,63,94}$ | | | | 0·246 abs$^{93}$ | |
| | | | | | 0·238 spect$^{94}$ | |
| | | | | | others$^{63,65}$ | |
| | | | | $\gamma$ | no $\gamma^{63,93}$ | |
| $^{34}$P | 12·4 s$^{96}$ | ('•') | $\beta^{-99}$ | $\beta^-$ | 5·1 (75%), 3·2 (25%) abs$^{96}$ | $Q_\beta - 5.1^7$<br><br>Refs.$^{100,7,101}$ |
| | 12·7 s$^{97}$ | B | excit$^{97}$ | $\gamma$ | 2·10, 4·0 (0·2%), no 3·22$_\gamma$ (lim 0·4%) | |
| | others$^{98}$ | | chem, excit, cross bomb$^{96}$ | | scint spect$^{32}$ | |

Refs. p. 1308

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## PRODUCTION AND PREPARATION OF PHOSPHORUS ISOTOPES

## METHODS OF PRODUCTION

Radioactive isotopes of phosphorus may be produced in a large variety of ways by subjecting suitable targets to bombardment by nuclear particles or $\gamma$-rays. The amount of energy liberated in any particular reaction is dependent on the difference in mass between the reactants and the products, and is known as the $Q$-value of the reaction. The main nuclear reactions in which phosphorus isotopes have been observed as products are given in Table I; the $Q$-values in this Table are taken from 1960 Nuclear Data Tables.[81] The feasibility of any nuclear reaction is to a large extent dependent on its $Q$-value, a high negative value indicating that only particles of very high energy could be effective. In general, the bombarding particle or photon will need more energy than is apparent from the $Q$-value, since there will be some

*Table I.—Nuclear Reactions for Production of Phosphorus Isotopes*

| Isotope | Nuclear reaction | Calculated[81] $Q$-value (Mev.) | Experimental threshold (Mev.) | References |
|---|---|---|---|---|
| $^{28}$P | $^{28}\mathrm{Si}(p, n)^{28}\mathrm{P}$ | −14·58 ± 0·30 | 15·6 ± 0·5[1, 3]<br>15·4 ± 0·6[2] | 1, 2, 3 |
| $^{29}$P | $^{28}\mathrm{Si}(p, \gamma)^{29}\mathrm{P}$ | 2·735 ± 0·011 | | 4 |
| | $^{28}\mathrm{Si}(d, n)^{29}\mathrm{P}$ | 0·510 ± 0·011 | | 5, 6, 7 |
| | $^{28}\mathrm{Si}(^{3}\mathrm{He}, d)^{29}\mathrm{P}$ | −2·758 ± 0·011 | | 8 |
| | $^{29}\mathrm{Si}(p, n)^{29}\mathrm{P}$ | −5·743 ± 0·010 | | 9 |
| | $^{31}\mathrm{P}(\gamma, 2n)^{29}\mathrm{P}$ | −23·643 ± 0·011 | 24·50[10] | 10 |
| $^{30}$P | $^{27}\mathrm{Al}(\alpha, n)^{30}\mathrm{P}$ | −2·652 ± 0·010 | 3·409[18]<br>≤ 3·056[20] | 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 |
| | $^{28}\mathrm{Si}(^{3}\mathrm{He}, p)^{30}\mathrm{P}$ | 6·345 ± 0·010 | | 21, 22, 23 |
| | $^{29}\mathrm{Si}(p, \gamma)^{30}\mathrm{P}$ | 5·585 ± 0·011 | | 24, 25, 26, 27, 28 |
| | $^{29}\mathrm{Si}(d, n)^{30}\mathrm{P}$ | 3·360 ± 0·011 | | 5 |
| | $^{30}\mathrm{Si}(p, n)^{30}\mathrm{P}$ | −5·030 ± 0·011 | | 29, 30 |
| | $^{31}\mathrm{P}(\gamma, n)^{30}\mathrm{P}$ | −12·316 ± 0·010 | 12·35 ± 0·2[34],<br>12·4 ± 0·2[35],<br>12·05 ± 0·2[36, 10]<br>12·33 ± 0·05[38] | 31, 32, 33, 34, 35, 36, 10, 37, 38 |
| | $^{31}\mathrm{P}(n, 2n)^{30}\mathrm{P}$ | −12·316 ± 0·010 | 12·3[40] | 39, 40 |
| | $^{31}\mathrm{P}(p, pn)^{30}\mathrm{P}$ | −12·316 ± 0·010 | | 41 |
| | $^{32}\mathrm{S}(\gamma, pn)^{30}\mathrm{P}$ | −21·178 ± 0·010 | 21·4[35] | 35 |
| | $^{32}\mathrm{S}(\gamma, d)^{30}\mathrm{P}$ | −18·954 ± 0·010 | 19·15 ± 0·20[35] | 35 |
| | $^{32}\mathrm{S}(n, 2np)^{30}\mathrm{P}$ | −21·178 ± 0·010 | | 42 |
| | $^{32}\mathrm{S}(d, \alpha)^{30}\mathrm{P}$ | 4·892 ± 0·010 | | 43, 44, 27, 45 |
| | $^{35}\mathrm{Cl}(\gamma, \alpha n)^{30}\mathrm{P}$ | −19·31 ± 0·01 | | 46 |
| $^{32}$P | $^{29}\mathrm{Si}(\alpha, p)^{32}\mathrm{P}$ | −2·4578 ± 0·0040 | | 47 |
| | $^{30}\mathrm{Si}(d, \gamma)^{32}\mathrm{P}$ | 12·9983 ± 0·0045 | | 48 |
| | $^{30}\mathrm{Si}(^{3}\mathrm{He}, p)^{32}\mathrm{P}$ | 7·5051 ± 0·0045 | | 22, 23 |
| | $^{31}\mathrm{P}(n, \gamma)^{32}\mathrm{P}$ | 7·9368 ± 0·0025 | | 49, 50, 51, 52 |
| | $^{31}\mathrm{P}(d, p)^{32}\mathrm{P}$ | 5·7120 ± 0·0024 | | 53, 54, 55, 56, 57 |
| | $^{32}\mathrm{S}(n, p)^{32}\mathrm{P}$ | −0·9258 ± 0·0021 | | 49, 58, 43, 59, 60, 61, 62, 40, 63, 64, 65, 66 |
| | $^{34}\mathrm{S}(d, \alpha)^{32}\mathrm{P}$ | 5·0811 ± 0·0037 | | 43, 27, 67, 68 |
| | $^{35}\mathrm{Cl}(\gamma, ^{3}\mathrm{He})^{32}\mathrm{P}$ | −19·6379 ± 0·0033 | | 46 |
| | $^{35}\mathrm{Cl}(n, \alpha)^{32}\mathrm{P}$ | 0·9393 ± 0·0033 | | 49, 69, 70, 71, 72 |
| | $^{37}\mathrm{Cl}(\gamma, \alpha n)^{32}\mathrm{P}$ | −17·97 ± 0·01 | | 46 |
| | $^{37}\mathrm{Cl}(p, p\alpha n)^{32}\mathrm{P}$ | −17·97 ± 0·01 | | 73 |
| $^{33}$P | $^{30}\mathrm{Si}(\alpha, p)^{33}\mathrm{P}$ | −2·970 ± 0·005 | | 74 |
| | $^{33}\mathrm{S}(n, p)^{33}\mathrm{P}$ | 0·5336 ± 0·0020 | | 74, 75, 76 |
| | $^{34}\mathrm{S}(\gamma, p)^{33}\mathrm{P}$ | −10·8872 ± 0·0045 | | 77 |
| | $^{35}\mathrm{Cl}(\gamma, 2p)^{33}\mathrm{P}$ | −17·2538 ± 0·0041 | | 77, 46 |
| | $^{37}\mathrm{Cl}(\gamma, \alpha)^{33}\mathrm{P}$ | −7·8572 ± 0·0040 | | 77, 46 |
| $^{34}$P | $^{34}\mathrm{S}(n, p)^{34}\mathrm{P}$ | −4·32 ± 0·20 | | 42, 78, 79 |
| | $^{37}\mathrm{Cl}(n, \alpha)^{34}\mathrm{P}$ | −1·29 ± 0·20 | | 80, 78, 79, 70, 72 |

transfer of momentum to the products, and since charged particles entering or leaving the nucleus have to surmount a Coulomb barrier. This minimum effective energy is the 'threshold' energy, and some experimentally determined values are given in the Table.

In addition to the reactions listed in Table I there are certain other nuclear processes which give rise to isotopes of phosphorus, usually together with a wide variety of other products. $^{32}P$ has been observed amongst the products of spallation of copper,[82-4] iron,[85] and other elements,[86-7] and $^{33}P$ has also been observed under these conditions.[86, 88] (Spallation is a nuclear process, resulting from bombardment with high energy particles, in which a number of fragments are produced.) $^{30}P$ and $^{32}P$ are formed during the bombardment of aluminium with $^{16}O$ and $^{14}N$ ions,[89-90] and $^{32}P$ has been detected in the proton-induced fission of lanthanum and gold.[84] The formation of $^{34}P$ by the reaction $^{79}Br(p, 2n)^{34}P^{44}Sc$ has been deduced from the observed threshold for the formation of $^{44}Sc$.[91] $^{32}P$ and $^{33}P$ have been found in rain water, and are believed to arise from the spallation of atmospheric argon by cosmic rays.[92-4]

The number of atoms of a product formed in a nuclear reaction is given approximately by:

$$N = I(1-e^{-n\sigma x})$$

where $N$ is the number of product atoms formed,
$I$ is the number of incident particles or photons,
$n$ is the number of target atoms per c.c.,
$\sigma$ is the cross section for the particular nuclear process in cm$^2$,
$x$ is the target thickness in cm.

For most reactions the cross-section is a complicated function of the energy of the bombarding particle, and its values under various conditions may be found in the references to Table I. However, the cross-section for irradiation by thermal neutrons usually varies inversely as the neutron velocity, and since the thermal neutron flux of a reactor is always quoted for an arbitrary velocity of 2200 m./sec. the use of the cross-section for neutrons of this velocity will give the thermal neutron contribution to the rate of formation of the product irrespective of the actual thermal neutron energies. Where reactions having positive $Q$-values are induced by neutron bombardment the absence of any barrier to neutrons enables thermal neutrons to take part in the reaction, and it can be seen from the data of Table I that only three of the nuclear reactions for the production of phosphorus isotopes are in this category: their thermal neutron cross-sections are[95]: $^{31}P(n, \gamma)^{32}P$, $190 \pm 10$ mb.; $^{35}Cl(n, \alpha)^{32}P$, $< 0{\cdot}05$ mb.; $^{33}S(n, p)^{33}P$, $15 \pm 10$ mb. (1 mb. = $10^{-27}$ cm.$^2$). For reactions induced by neutrons of higher energy, graphs showing the variation of cross-section with neutron energy are given by Hughes and Schwartz.[95]

With the exception of $^{32}P$ and $^{33}P$ the radioactive isotopes of phosphorus have very short half-lives, and are therefore of little practical use. From the point of view of nuclear properties one might expect $^{32}P$ and $^{33}P$ to be of about equal importance, but the difficulties inherent in $^{33}P$ production have resulted in $^{32}P$ being the only isotope of importance.

## PREPARATION OF $^{32}$P

Of the nuclear reactions given in Table I there are three that are induced by neutrons, and since nuclear reactors provide an abundant and relatively cheap supply of neutrons these are the reactions used for the production of $^{32}P$. The $^{31}P(n, \gamma)^{32}P$ reaction yields radiophosphorus in the presence of a large amount of inactive phosphorus, from which it can be separated to a considerable extent in suitable cases; on the other hand the $^{32}S(n, p)^{32}P$ and $^{35}Cl(n, \alpha)^{32}P$ reactions produce $^{32}P$ in a carrier-free condition, that is with no inactive phosphorus present except for the small amount which may have been present as an impurity in the target material. A number of other nuclear reactions will take place giving rise to other radioactive species, but by chemical separation all impurities other than phosphorus isotopes can be removed. (Thus Fermi[49] separated radiophosphorus by chemical processes from the products of all three neutron-induced reactions. For the separation of radiophosphorus from irradiated sulphuric acid or from a solution of irradiated ammonium chloride in dilute nitric acid, sodium phosphate was added as a carrier and the phosphorus was precipitated as a phosphomolybdate. Irradiated phosphoric acid was diluted and treated with sulphuric acid and sodium silicate; the silicate was then converted to an insoluble form which carried the radiophosphorus.) Other phosphorus isotopes will very rapidly decay to insignificant levels with the exception of $^{33}$P which is present to the extent of about 1% or less in the radiophosphorus produced from sulphur as a result of the $^{33}S(n, p)^{33}P$ reaction.

### The $^{32}S(n, p)^{32}P$ Reaction

This is the most important reaction for the production of $^{32}$P. Early attempts to obtain radiophosphorus by this process involved the use of neutrons emitted by radium–beryllium sources, and in view of the very small flux available the amounts produced were very small. The target material in these early experiments was usually carbon disulphide, which was used by Alikhanov[96] at about the same time as Fermi carried out the separations from sulphuric and phosphoric acids and from ammonium chloride. Govaerts showed that by simultaneous irradiation and electrolysis of carbon disulphide between copper electrodes radiophosphorus was deposited on the electrodes, and could be recovered by treatment with nitric acid[97–8]; an increase in weight of the anode was observed[97] which could not be due to the minute amounts of radiophosphorus formed, and appears to have arisen from the deposition of decomposition products of carbon disulphide.[98] Oxidation of the radiophosphorus to phosphoric acid by means of bromine, and extraction from the organic phase with water after the addition of inactive phosphoric acid as carrier, enabled sources of any desired activity and weight to be produced.[99] Carrier-free $^{32}$P was obtained by the irradiation of a solution of white phosphorus in carbon disulphide; the white phosphorus was converted to insoluble red phosphorus during the irradiation, and radiophosphorus produced was absorbed by the precipitate and could be separated from it by extraction with water.[100] The $^{32}$P in this case could be formed by both the $^{32}S(n, p)^{32}P$ and the $^{31}P(n, \gamma)^{32}P$ reactions. In an extensive review[101] Govaerts has described a great deal of the early work on radiophosphorus preparation, and has discussed those properties of phosphorus-32 which were known at that time. A later review by Dzantiev and Neĭman[101a] includes an extensive bibliography.

### Methods of Separation

Other methods used for the separation of radiophosphorus from irradiated carbon disulphide include precipitation as ferric phosphate,[102] removal of the carbon disulphide by distillation,[102] and extraction of the phosphorus by nitric acid in the presence of air and a small amount of iodine.[103] The radiophosphorus can be recovered from the aqueous medium by precipitation as a phosphomolybdate or as magnesium ammonium phosphate in the presence of a phosphate carrier. In more recent work a combination of these techniques has been employed[104]: extraction with nitric acid, hydrogen peroxide, water, or 10% sodium hydroxide solution gave yields of 70 to 80%, and these are increased by distillation of the carbon disulphide during the last stages of the extraction process. The electrolytic method of separation has been applied more recently to carbon disulphide irradiated by neutrons from a Cockcroft–Walton machine.[105]

A few investigations have been carried out on the separation of radiophosphorus from other sulphur compounds. McIsaac and Voigt[106] developed a method of separation from irradiated sodium sulphate by adsorption on a cation exchange resin which has been saturated with iron and subsequently treated with ammonium hydroxide. The phosphorus was removed from the column by elution with sodium hydroxide solution and the solution was then passed through a second ion exchange column, this time in acid form, in order to remove the sodium ions.

Radiophosphorus is adsorbed when a solution of an irradiated salt such as a sulphate or sulphite is passed through an alumina column.[107-8] The target salt can be removed from the column by treatment with ammonium hydroxide and hydrogen peroxide. This does not appreciably affect the adsorbed phosphorus which can then be desorbed by sodium hydroxide. Another possible adsorbent is magnesium oxide,[107] which can subsequently be dissolved in acid; magnesium ions can then be removed by ion exchange. If magnesium sulphate is used as the target material and a solution of the target is then treated with ammonium hydroxide, the suspension of magnesium hydroxide formed acts as an adsorbent and the adsorbed phosphate can subsequently be recovered in the same way as from magnesium oxide.[108]

Korshunov and Shafiev[109] found that radiophosphorus can be extracted from irradiated sulphur monochloride by adsorption on an air-dried silica-gel column. The target material is eluted with carbon tetrachloride and the phosphorus obtained in 95% yield by elution with acidified water.

Although some of these methods are convenient for the preparation of small quantities of radiophosphorus in the laboratory, they are not readily adapted for large scale production. The most suitable target material for bulk irradiation in a reactor is elemental sulphur, and a number of processes have therefore been devised for the extraction of radiophosphorus from irradiated sulphur.

### EXTRACTION FROM A MELT

The first method of producing large amounts of radiophosphorus by this process involves pouring molten sulphur into boiling concentrated nitric acid.[110] The aqueous phase, which contains nearly all the phosphorus together with a little sulphuric acid and other impurities, is evaporated to dryness and taken up in water to which a little hydrochloric acid is added. The phosphorus is then removed from the solution by co-precipitation with ferric hydroxide, and finally freed from the iron by means of a cation exchanger, or by extraction of the iron into *iso*propyl ether from a solution in 9 N. hydrochloric acid.

This method did not prove to be very satisfactory in practice and was difficult to adapt to remote operation, and it therefore underwent a series of modifications. Instead of the sulphur being melted and then poured into boiling acid it was melted and mixed with 16 N. nitric acid in an autoclave, and for the subsequent separation of phosphorus by co-precipitation lanthanum hydroxide was used instead of ferric hydroxide. (The small amount of iron present as an impurity in the nitric acid phase was removed as the hydroxide before the lanthanum was added, the precipitation being carried out at a pH of over 11 so that phosphorus would not be co-precipitated.) An ion exchanger was used to separate the lanthanum from the radiophosphorus, which was obtained in a carrier-free solution as phosphoric acid.[111] Kenny and Spragg[112] suggested that adsorption of the phosphorus on dialyzed iron in the presence of a suitable amount of sulphate, instead of co-precipitation with a trivalent metal hydroxide, would lead to separation of the phosphorus from chromium and aluminium, which are present as impurities if stainless steel equipment is used, and which interfere in the final purification step by retaining some of the phosphorus on the ion-exchange column.

Meanwhile it was found by Butler[113] that the use of dilute nitric acid, under sufficient pressure to raise its boiling point to the melting point of sulphur, gives yields comparable with those obtained by the use of concentrated acid but gives rise to far less corrosion products from the autoclave. The purification process follows the same lines as in the Cohn method, and it is found that better yields can be obtained with lanthanum hydroxide as a carrier than with ferric hydroxide. This method, with slight modifications, has been extensively used for the large scale production of radiophosphorus at Oak Ridge in the U.S.A.[114] and at Harwell in Great Britain.[115-7] A rocking autoclave, described by Arrol,[116] was brought into use at Harwell; this was used for mixing the two phases during the extraction process, and was provided with a ridge dividing the base into two compartments so that the sulphur could be allowed to solidify in one of them and the aqueous layer then decanted into the other. The use of a container of borosilicate glass inside the pressure vessel and the elimination of metal parts of the apparatus wherever possible greatly reduce the difficulties of purification of the product.

Another reagent which has been used for the extraction stage is acetic acid to which sufficient acetic anhydride has been added to bring its boiling point to the melting point of sulphur.[118] The mixture is refluxed and mixed by a current of air, and the aqueous layer is then separated and distilled. The subsequent purification steps are similar to those already described, but the overall yield is only about 80% and the technique imposes some limitations on the amount of sulphur which can be handled. However, by an alternative purification procedure, involving evaporation to dryness of the extract solution followed by leaching of the radiophosphorus with dilute mineral acid, yields of over 90% can be attained.[119]

### EXTRACTION FROM A SOLUTION

In this method the mass of irradiated sulphur is dissolved in a suitable organic solvent and the phosphorus can then be extracted by an aqueous reagent. A wide variety of organic solvents can be used: these include tetrachlorethane, tetrabromoethane, dichloroethylene,[120] trichloroethylene,[120-1] chloroform,[109] carbon disulphide,[120,122] and toluene.[123,109] In one process[120] the radiophosphorus is extracted by a halogen acid, the yield at this stage being 60–89%. About 25% of this material is lost during the purification procedure, in which metallic impurities are removed on an ion-exchange column and the product is treated with hydrogen peroxide. Yields of about 90% can be obtained by using double-distilled water as the extracting agent.[123] The aqueous solution is then evaporated to dryness and treated with hydrogen peroxide, and the phosphorus which has been adsorbed on the walls of the evaporator is desorbed by dilute hydrochloric acid. The resulting product contains less than 1% of impurities.

A process which has been proposed for use in Japan[122] involves extraction of the radiophosphorus from a solution of irradiated sulphur in carbon disulphide; for this purpose dilute ammonium hydroxide solution was found to be the best reagent. The aqueous solution is evaporated to dryness and the product taken up in fairly concentrated nitric acid. After being evaporated again and taken up in dilute hydrochloric acid it is purified by means of ion exchange columns. An alternative method of purification involves extraction of the radiophosphorus with butyl acetate in the presence of ammonium molybdate followed by back extraction with water. The phosphomolybdate is then removed by extraction with tributyl phosphate. Yields of over 90% can be obtained by either procedure.

Poczynajło and Campbell[121] have suggested a procedure by which the irradiated mass of sulphur (carefully purified before irradiation) is digested with very dilute hydrochloric acid under reflux for an hour before the solvent is added. The mixture is then refluxed for a further half hour after which the organic solvent is distilled off and the product filtered and purified. The best solvent for this process was found to be trichloroethylene with which yields of $\sim 90\%$ can be obtained.

It is possible to extract radiophosphorus by adsorption from a solution of irradiated sulphur in carbon disulphide. Possible adsorbents include alumina[124] and silica gel.[125] A production process based on adsorption has been suggested[125]; the sulphur is converted into the $\alpha$ form before irradiation so that the irradiated mass is completely soluble in carbon disulphide. The solution in carbon disulphide is passed through a column of adsorbent and the small amount of sulphur adsorbed is eluted with pure carbon disulphide; the radiophosphorus is then removed by a suitable reagent. The best eluant was found to be 5 N. nitric acid and the best adsorbent silica gel, treated with ammonium hydroxide, hydrochloric acid, and water, and then dried by a current of air. With these reagents a yield of 80% can be obtained.

### EXTRACTION BY DIFFUSION

During the transformation of sulphur from the rhombic to the monoclinic form radiophosphorus diffuses rapidly from the sulphur grains and can be extracted with boiling water. Powdered sulphur, of grain size less than 5μ, is purified by treatment with hydrochloric acid, irradiated, and then washed with hot water containing *sec.*-octyl alcohol as a wetting agent. This washing process removes radioactive impurities from the surface of the sulphur grains, but does not extract the radiophosphorus to any appreciable extent. (The chief impurities concerned are $^{35}$S in water-soluble forms such as sulphuric acid, and active material which has recoiled from the irradiation cans.) The sulphur is then mixed with water and a small amount of *sec.*-octyl alcohol and the mixture is boiled for an hour or more, after which the alcohol is distilled off. The resulting aqueous solution is separated from the sulphur by filtration and evaporated to a suitable volume.[126-8] In an earlier purification procedure, designed for use with other wetting agents, the mixture was evaporated to dryness and organic matter was destroyed with nitric acid, after which the phosphorus was taken up in water.[129] The yield of radiophosphorus obtained by this process is only about 76% if sublimed sulphur is used, but can be increased to 93% if 5μ-micronized sulphur is used.

### EXTRACTION BY DISTILLATION

When an irradiated mass of sulphur is distilled in a nitrogen atmosphere the residue contains all the radiophosphorus. This is refluxed for an hour with very dilute hydrochloric acid and a little hydrogen peroxide to remove traces of organic matter, and a very high yield of radiophosphorus is obtained as a solution of phosphoric acid. This process, which is ideally suited to remote control, has the advantage of producing no radioactive waste, and the distilled sulphur, being in a very high state of purity, can be re-irradiated without further treatment.[130-1]

### EXTRACTION BY RECOIL

In the course of a nuclear reaction in which a particle or photon is emitted the product nucleus recoils some distance from its original position. In the case of the $^{32}S(n, p)^{32}P$ reaction the recoil distance may be up to 0·65 μ,[132] and therefore if very small particles are irradiated an appreciable proportion of the product atoms escape and can be stopped in an inert receiver in which the particles are suspended. The $^{35}$S produced as a by-product by the $^{34}S(n, \gamma)^{35}S$ reaction has a very much smaller recoil range and therefore very little of it can leave the sulphur particles. As a result the radiophosphorus is obtained more or less free from radiosulphur. $^{32}$P has been obtained carrier-free in this way with water as the receiver,[131-2] but the yield is small and the method does not form a satisfactory basis for a production process.

## Other Methods of Purification and Concentration of $^{32}$P

In addition to the purification methods already mentioned a few processes have been described which could be used in the production of radiophosphorus. The separation of phosphate ions from iron ions can be achieved by the precipitation of iron as the hydroxide followed by precipitation of bismuth phosphate.[143-4] The bismuth phosphate precipitate is then dissolved in a halogen acid and the bismuth removed by the precipitation of bismuth sulphide with hydrogen sulphide or by the hydrolysis of bismuth salt.

Carrier-free radiophosphorus can be concentrated from a solution of orthophosphate by adsorption on ignited barium sulphate.[145] Other cations are retained in solution during the adsorption stage by the addition of a calculated amount of ammonium hydroxide, and the radiophosphorus is subsequently desorbed by a small amount of very dilute hydrochloric acid and purified by treatment with an ion-exchange resin. The yield from this process is about 95%.

### The $^{31}P(n, \gamma)^{32}P$ Reaction

Since this reaction produces $^{32}P$ in the presence of a large amount of inactive phosphorus it is not generally used for the preparation of carrier-free $^{32}P$, but it is a convenient process to use when there is no objection to the presence of carrier. One important advantage is that the product does not contain $^{33}P$, which is formed when sulphur is irradiated. The target is usually red phosphorus, and as there are no significant radioactive by-products no elaborate chemical processing is required.

Although the irradiation of phosphorus compounds is not a satisfactory method for the production of carrier-free radiophosphorus, the active product can be separated from the target material in certain cases, since the recoil of the product nucleus often results in the breaking of chemical bonds and the formation of different compounds. Thus neutron irradiation of triphenyl phosphate in benzene solution yields $^{32}P$ partly in ionic form, which can be extracted by water,[134] and $^{32}P$ may also be extracted by water from a solution of irradiated triphenylphosphine in benzene.[135] The best reagent for the extraction of radiophosphorus from irradiated tributyl phosphate has been found to be potassium hydroxide of pH 12·5, which gives a yield of over 50%.[136] Another compound which may be used for the preparation of carrier-free $^{32}P$ is triphenylphosphine oxide. The radiophosphorus can be extracted by water from a solution of this target in chloroform, or can be co-precipitated with ferric hydroxide by means of ammonium hydroxide from an alcoholic solution, the phosphorus then being separated from the iron on an ion-exchange column.[137]. The difficulty with all these processes is that the organic compounds are likely to undergo extensive decomposition under reactor irradiation, and the method is therefore unsuitable for large scale production.

### The $^{35}Cl(n, \alpha)^{32}P$ Reaction

Although carrier-free $^{32}P$ can be produced by this reaction the yields are very small and the radiophosphorus must be separated from large amounts of other radioactive species. The reaction has therefore not been used in any production process, but radiophosphorus can be extracted from irradiated chlorine compounds in a number of ways. Simultaneous irradiation and electrolysis of carbon tetrachloride results in partial deposition of radiophosphorus on the electrodes,[98] and adsorption of the $^{32}P$ on silica gel or on the walls of the irradiation vessel is an alternative separation procedure.[109] Adsorption on the vessel walls may be as high as 80–90% if the carbon tetrachloride contains a trace of water. Separation of the $^{32}P$ from irradiated ammonium chloride can be achieved by co-precipitation with aluminium or ferric hydroxides or with barium sulphate. Other carriers can be used but do not give such good yields.[109] The recoil range of $^{32}P$ atoms in sodium chloride is about 0·5 $\mu$,[138] and therefore separation by recoil may be achieved from a finely powdered target material. Silica and naphthalene have been used as receivers,[133, 138] but only about 1% of the radiophosphorus is recovered.

## PREPARATION OF $^{33}P$

Although $^{33}P$ could have many applications in science and medicine, it has not so far been produced commercially. In principle any of the reactions given in Table I could be used for its production, but the only reaction by which it could be produced in a nuclear reactor is $^{33}S(n, p)^{33}P$. As production by means of an accelerator is very costly, the $^{33}S(n, p)^{33}P$ reaction would seem to be the most promising method; the difficulty is that $^{33}$S is present in natural sulphur only to the extent of 0·75%, so that under pile irradiation a very small amount of $^{33}$P is obtained together with a very large amount of $^{32}$P. Because of the positive $Q$-value for the reaction it is possible to produce $^{33}$P by means of thermal neutrons,[74] which should not give rise to the $^{32}S(n, p)^{32}P$ reaction, but it is difficult in practice to eliminate the higher energy neutrons completely without sacrificing most of the available thermal flux. The problem is therefore one of choosing the best of a number of difficult methods, which may be summarized as:

(1) Production by means of an accelerator. This would be very expensive and simultaneous production of $^{32}$P is very probable.
(2) Irradiation in a pure thermal flux. The difficulty here is one of obtaining a high enough flux with complete elimination of higher energy neutrons. It might be possible to produce small quantities of pure $^{33}$P in this way.[139]
(3) Extraction of $^{33}$P from the mixture produced by pile neutrons by some form of isotope separation technique.
(4) Elimination of most of the $^{32}$P from the mixture produced by pile neutrons by radioactive decay. The snag is that the half-lives are similar, so that there would be very little $^{33}$P left after this process unless the starting material were fairly rich in $^{33}$P.
(5) Preliminary enrichment of $^{33}$S in the sulphur target followed by reactor irradiation.

The advantages and disadvantages of each of these methods have been considered by Westermark,[140] who concluded that the last of these methods was the most promising, in that an enriched sulphur target could be used repeatedly, so that the cost of enrichment would be distributed over many batches of $^{33}$P. By elution of bisulphite ions with hydrochloric acid from an anion exchange resin an appreciable enrichment of $^{33}$S can be achieved,[141-2] and repetition of this process should yield a target material of satisfactory purity. Recovery of $^{33}$P from the sulphur target after irradiation could be carried out in the same way as in the preparation of $^{32}$P.

## PREPARATION OF $^{30}$P

Although it has a half-life of only 2·5 min., $^{30}$P has been obtained in a carrier-free condition by means of the $^{31}P(\gamma, n)^{30}P$ process, the target material being finely powdered red phosphorus mixed with tetralin. After irradiation the inactive phosphorus is filtered off, leaving the $^{30}$P in the tetralin into which it has recoiled during the irradiation.[133,143] The recoil distance, which does not exceed 0·25 $\mu$, has been calculated from the yield and the particle size of the target material for various photon energies.

## PREPARATION OF COMPOUNDS CONTAINING $^{32}$P

Because the formation of radiophosphorus is often accompanied by the rupture of chemical bonds, labelled compounds cannot usually be prepared directly by the irradiation of the corresponding inactive compounds. In some cases part of the radiophosphorus is found in the same chemical form as the target material, and the labelled compound may then be obtained by a careful purification process, but it is usually more convenient to synthesize the required compound from radiophosphorus in the form of the element or of one of its simplest compounds. A number of these syntheses have been described and brief outlines of some of them will be given here as examples of the techniques used. Many labelled compounds are commercially available, and a comprehensive list is given in Radioisotopes, Vol. II.[146] A useful compilation of inorganic syntheses has recently been published.[146a]

Refs. p. 1319

## Preparation of Phosphates

The radiophosphorus obtained from irradiated sulphur is usually found to be mainly in the form of orthophosphate, but various methods have been adopted for the preparation of pure labelled phosphates. Pure disodium orthophosphate has been prepared by warming irradiated red phosphorus with hydrogen peroxide and neutralizing with sodium hydroxide.[147] The red phosphorus used in this work was contaminated with copper during the irradiation, and this was removed by electrolysis before neutralization. Other methods of preparation were not found to give such a high degree of purity. Pure labelled magnesium ammonium phosphate was prepared by Fiskell[148] from irradiated calcium phosphate. The target material was treated with a mixture of ammonium persulphate and perchloric acid, the product diluted and neutralized, and radiophosphorus precipitated as phosphomolybdate. After purification by re-precipitation the molybdate was dissolved in hydrochloric acid and magnesium ammonium phosphate precipitated. This was redissolved and the precipitation step repeated, and the final product was washed with alcohol and ether.

Colloidal suspensions of chromic phosphate have been prepared by boiling a mixture of phosphoric acid, chromic acid, and sodium sulphite solution in the presence of gelatin.[149] Methods of preparation of ortho-, meta-, and pyro-phosphoric acids have been described by Hull,[150] and the preparation of labelled fertilizers (such as superphosphate) has been described by Hill, Fox, and Mullins.[151]

### PREPARATION OF BARIUM DIHYDROGEN HYPOPHOSPHATE

Small portions of irradiated red phosphorus were added to an alkaline solution of potassium permanganate, the mixture was heated for an hour and the manganese dioxide was then filtered off and washed. Glacial acetic acid was added to the filtrate, the mixture was heated to boiling, and barium dihydrogen hypophosphate was precipitated by the gradual addition of barium chloride.[152]

## Preparation of Phosphorous Acid

Labelled phosphorus trichloride was prepared by refluxing irradiated red phosphorus with inactive phosphorus trichloride and pentachloride. The labelled phosphorus trichloride was separated by fractional distillation, added to carbon tetrachloride, and treated with water at $-5°$C. The hydrogen chloride formed was removed by warming to room temperature and washing with carbon tetrachloride, and after filtration the product was warmed to 60°C. under vacuum to extract the last traces of hydrogen chloride.[152]

## Preparation of Phosphorus Chlorides and Oxychloride

A mixture of radioactive phosphorus pentachloride and oxychloride has been produced by passing a stream of chlorine over a heated mixture of charcoal and labelled calcium phosphate and pyrophosphate.[153] From the product phosphorus trichloride was prepared by reduction of the pentachloride with powdered antimony followed by distillation of the trichloride-oxychloride mixture, the vapour being passed over heated charcoal which reduced the oxychloride to trichloride.[153] Another method of preparation of the trichloride[152] has already been mentioned, and phosphorus oxychloride has also been produced by the reaction of labelled orthophosphoric acid with inactive phosphorus pentachloride at a low temperature[154-5] and by the reaction of labelled ferric phosphate with carbonyl chloride.[156]

## Preparation of Organic Compounds Labelled with Phosphorus-32

Full details of the syntheses which had been reported by 1955 have been given in Volume II of *Organic Syntheses with Isotopes*,[157] and a useful bibliography is given by Charlton.[158] Compounds for which syntheses have recently been reported include glycerophosphates,[159-60] glucose-1-phosphate,[159] uridine 5′-phosphate,[161] disodium $\alpha$-naphthylphosphate,[154] adenosine triphosphate,[162-4] *iso*propyl methylphosphonofluoridate,[165] and some thiophosphate derivatives.[166-7] For some of these syntheses biological processes have been used.

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## THE EXCITED-ATOM CHEMISTRY OF PHOSPHORUS

In most nuclear reactions a considerable amount of energy is released, and this is in general far in excess of chemical bond energies. In bombardment by charged particles or fast neutrons kinetic energy is imparted to the target nucleus, and if particles are emitted in the reaction the resulting nucleus will recoil from its original site. In either case the nucleus is likely to have sufficient energy for any chemical bonds to be ruptured. In $n, \gamma$ reactions brought about by thermal neutrons the energy imparted by the incident neutron is not sufficient to cause bond rupture, but the $\gamma$-rays emitted have momentum $E_\gamma/c$, where $E_\gamma$ is the $\gamma$-ray energy and $c$ the velocity of light. The conservation of momentum results in the product atom recoiling with an energy of $E_\gamma^2/2Mc^2$, where $M$ is the mass of the atom in atomic mass units. For a phosphorus atom this means that the recoil energy for a 1 Mev. $\gamma$-ray will be about 17 ev., and as most chemical bond energies are between 1 and 5 ev. emission of a $\gamma$-ray of this energy would be expected to lead to bond rupture. It may happen, however, that two or more $\gamma$-rays are emitted in different directions, and in this case bond rupture may not follow.

The first chemical reaction observed to arise from a recoil process was the breakdown of ethyl iodide on neutron irradiation, the radioactive $^{128}$I appearing mainly in a form which could be extracted with water.[1] Reactions of this type, in which the target and product are isotopes of the same element, are referred to as Szilard-Chalmers reactions, and have frequently been used for the preparation of carrier-free radioisotopes. In many cases, although the radioactive product is initially formed in a form which differs chemically from the target material, only a very small fraction of it can be separated radiochemically because recombination occurs under the conditions of the irradiation.[2] Reaction of the radioactive atoms with the target material may also lead to the formation of new compounds,[3] so that in a given reaction a variety of new products may be found, together with a certain amount of apparently unchanged target material incorporating the radioactive isotope. 'Excited-atom' or 'hot-atom' chemistry is concerned with the study of the chemical changes which occur as a result of these nuclear processes.

We may also consider under this heading the chemical effects resulting from those nuclear reactions in which there is a change of atomic number. There must be a chemical change here since the target and product atoms are not of the same element. In addition recoil effects are much greater than they are for $n, \gamma$ reactions and can result in some of the product atoms leaving a powdered target,[4] and the excited state of the product atom can lead to its appearance in unexpected chemical forms.[5]

As only a very small proportion of the atoms of the target element are transformed in these reactions (except in the case of extended irradiations by neutrons in nuclear reactors), the chemical products are present only in trace amounts, and must usually be detected by means of their radioactivity. The usual method of isolation of the products involves the addition of carriers followed by chemical separation[6]; the various fractions are then examined for their radioactivity. This method has two disadvantages: firstly that the addition of carriers and the subsequent chemical operations may lead to further chemical changes in the products of the nuclear reaction, and secondly that unexpected or unknown products will be overlooked since they will usually follow one or other of the carriers added, and will be mistakenly assigned to that chemical form. Of the alternative methods available for the separation of the products, the method of paper electrophoresis or paper electrochromatography has proved of particular value in the study of the excited-atom chemistry of phosphorus,[7-9] and has revealed the presence of some products which have not yet been identified.[9]

For general discussions of the theoretical basis and methods of excited-atom chemistry reference should be made to standard works on radiochemistry[6,10] and to a review of the subject.[11]

The isotopes $^{28}$P, $^{29}$P, and $^{34}$P have very short half-lives, and their chemical forms have therefore not been investigated.

## EXCITED-ATOM CHEMISTRY OF $^{30}$P

Very little is known about the chemical forms in which $^{30}$P is produced. However, when red phosphorus is finely powdered and mixed with tetralin, and then subjected to $\gamma$ irradiation, some of the radioactive phosphorus formed by the $^{31}P(\gamma, n)^{30}P$ reaction is found in a carrier-free condition in the tetralin.[4,12] From the particle size of the target material and the fraction recovered from the tetralin the recoil distance has been calculated for the $\gamma$-energies used.

*Table II.—Recoil Range of* $^{30}$P *Produced by the* $^{31}P(\gamma, n)^{30}P$ *Reaction*[4]

| Max. $\gamma$ energy (Mev.) | 18 | 20 | 22 | 23 |
|---|---|---|---|---|
| Calculated mean recoil energy (Mev.) | 0·16 | 0·27 | 0·36 | 0·40 |
| Range ($\mu$) | 0·08 | 0·10 | 0·18 | 0·23 |
| Range ($\mu$g/cm.$^2$) | 19 | 23 | 42 | 54 |

The experimental results show a wide scatter, and therefore the values of the recoil range are subject to considerable error.

The first row of Table II gives the maximum $\gamma$-energy for each irradiation, the second row gives very approximate computed values for the mean recoil energies, and the last two rows give the observed recoil ranges in microns (for red phosphorus) and in micrograms per square centimetre. The second way of expressing the range is particularly useful, since the range of any particle in terms of the mass per unit area of the stopping medium is independent of the density of that medium.

## EXCITED-ATOM CHEMISTRY OF $^{32}$P

This aspect of the radiochemistry of phosphorus has been extensively studied, and has proved to be of considerable complexity. We shall deal first with the estimates which have been made of the recoil range, and then with the chemistry of the reactions $^{31}P(n, \gamma)^{32}P$, $^{32}S(n, p)^{32}P$, and $^{35}Cl(n, \alpha)^{32}P$ in turn. For the $^{31}P(n, \gamma)^{32}P$ reaction the irradiation of inorganic and of organic compounds will be treated separately.

## THE RECOIL RANGE OF $^{32}$P

On neutron irradiation of finely powdered sulphur suspended in water a considerable fraction of the radiophosphorus produced appears in the liquid phase from which it can be recovered.[4, 13] Similar separations can be achieved by the irradiation of sulphur or potassium sulphate intimately mixed with solid receivers, and by the irradiation of ammonium chloride mixed with silica.[4] In these experiments either the target or the receiver is soluble in dilute acid, so that the fraction of the radiophosphorus appearing in the receiver can be readily determined. With sodium chloride as target and naphthalene as receiver it was found necessary to arrange them in alternate layers for irradiation. The yield of $^{32}$P in the receiver is then only about 1%, but nevertheless the recoil range can be calculated.[14] In Table III are given details of the neutron energies used, the mean phosphorus recoil energies, and the observed recoil ranges for a number of experiments.

Subsidiary experiments showed that during the irradiation of sulphur suspended in water no appreciable diffusion of phosphorus from the sulphur grains occurred and very little sulphur entered the aqueous phase.

## CHEMICAL STATE OF $^{32}$P PRODUCED BY THE $^{31}P(n, \gamma)^{32}P$ REACTION

### IRRADIATION OF INORGANIC COMPOUNDS

The early work on the chemical state of the radiophosphorus produced by neutron bombardment of inorganic phosphorus compounds was mainly confined to the determination of the fractions of the radioactive phosphorus atoms which were 'retained' in the original chemical form on irradiation of phosphorous and phosphoric acids and their salts. The fractions 'retained' included all active phosphorus found in the original form, and much of this could well have arisen by recombination of fragments or by exchange of the active atoms with the inactive atoms of the unchanged target material. Moreover, these reactions could have been brought about either thermally or as a result of the excited state of the active atoms. However, it has been shown by Wilson[15] that thermal exchange between phosphate and phosphite is very small under a wide variety of conditions, and Hull[16] showed that exchange between ortho-, pyro-, and meta-phosphates does not occur. The results of Libby's experiments on phosphorus retention are given in Table IV.[17] From the constancy of the retention shown by phosphates under various conditions it is concluded that the retention is determined by the initial recoil process and not by any of the subsequent processes outlined above. As the radiophosphorus was separated into only two fractions (carried by phosphite and phosphate) no other species could be observed, but Libby considered that any phosphorus formed in the +4 state would be oxidized to the +5 state in aqueous solution.

*Table III.—Recoil Ranges of* $^{32}$P *Produced by the* $^{32}$S($n$, $p$)$^{32}$P *and* $^{35}$Cl($n$, $\alpha$)$^{32}$P *Reactions*[4, 13–4]

| Reaction | Target | Receiver | Neutron energy | Recoil energy (Mev.) | Percentage of $^{32}$P in receiver | Recoil range | | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | (μ) | (μg/cm$^2$) | |
| $^{32}$S($n$, $p$)$^{32}$P | S | Water | Pile neutrons | | 35 | 0·37 | 77 | Dilute suspension. |
| | S | Water | Pile neutrons | | 25 | | | 0·1 g. S/cc. |
| | S | Water | 11 Mev. (max) | 0·6 | 75 | 0·65 | 135 | |
| | S | $MgCO_3$ | | | | | | Receiver soluble in acid. |
| | S | $(NH_4)_2CO_3$ | | | | | | Receiver soluble in water. |
| | $K_2SO_4$ | MgO | | | | | | Target soluble in water. |
| $^{35}$Cl($n$, $\alpha$)$^{32}$P | NaCl | Naphthalene | Pile neutrons | 0·59 | 1 | 0·5 | 105 | Receiver soluble in benzene. |
| | $NH_4Cl$ | $SiO_2$ | Pile neutrons | 0·59 | 50 | 0·7 | 107 | Target soluble in water. |

*Table IV.—Amounts of Radiophosphorus retained in the Original Chemical form*[17]

| Target | Post-irradiation treatment | Retention (%) |
|---|---|---|
| $Na_2HPO_3,5H_2O$ | Dissolved in water | $92 \pm 3$ |
| $NaH_2PO_4,H_2O$ | ,, ,, ,, | $45 \pm 4$ |
| $Na_2HPO_4,12H_2O$ | ,, ,, ,, | $52 \pm 3$ |
| $Na_3PO_4,12H_2O$ | ,, ,, ,, | $50 \pm 4$ |
| $Na_3PO_4,12H_2O$ | ,, ,, 1 N. NCl | $51 \pm 4$ |
| $Na_3PO_4,12H_2O$ | ,, ,, 1 N. NaOH | $53 \pm 4$ |
| $Na_3PO_4,12H_2O$ | ,, ,, 6 N. NaOH | $47 \pm 4$ |
| 0·83 M. $H_3PO_4$ | | $43 \pm 3$ |
| 0·96 M. $H_2PO_4^-$ | | $54 \pm 8$ |
| 0·32 M. $HPO_4^{2-}$ | | $38 \pm 3$ |
| 0·58 M. $PO_4^{3-}$, 0·28 M. $OH^-$ | | $32 \pm 2$ |

*Table V.—Chemical Forms of* $^{32}P$ *in Neutron-irradiated Orthophosphates*

| Target | Retention (%) | Percentage of $^{32}P$ found as | | | | Reference |
|---|---|---|---|---|---|---|
| | | Phosphite and hypophosphite | Hypophosphate | Pyrophosphate | Metaphosphate | |
| $Na_2HPO_4$ | < 50 | | | | | 18 |
| $Na_2HPO_4$ | 23 | 46 | | 31[a] | | 19 |
| $Na_2HPO_4,2H_2O$ | 22 | 52 | | 25[a] | | 19 |
| $KH_2PO_4$ | 88–100 | 0–12 | | | | 20 |
| $KH_2PO_4$ | 79–95 | | | [b] | [b] | 21 |
| $KH_2PO_4$ | > 81 | | | | | 22 |
| Monocalcium phosphate | 30–43 | | 34–45 | 16 | | 23 |
| Tricalcium phosphate | 38 | | 36 | | 32 | 23 |
| Tricalcium phosphate | 48–57 | | | | | 22 |

[a] On hydrolysis 7% appeared in phosphite fraction.
[b] 4–21% found as dehydrated forms of phosphate.

*Table VI.—Chemical Forms of* $^{32}P$ *in Irradiated Phosphorus Compounds*

| Target | Percentage of $^{32}P$ found as | | | | | Reference |
|---|---|---|---|---|---|---|
| | Orthophosphate | Phosphite and hypophosphite | Hypophosphate | Pyrophosphate | Metaphosphate | |
| $Na_2HPO_3,5H_2O$ | 12 | 74 | | 15[a] | | 19 |
| $Na_4P_2O_7$ | 11 | 30 | | 59[a] | | 19 |
| $Na_4P_2O_7,10H_2O$ | 36 | 20 | | 45[a] | | 19 |
| Calcium pyrophosphate | 0·7–14 | | 20–30 | 50–59 | 15 | 23 |
| Calcium hypophosphite | | | present | | | 24 |
| Superphosphate | | | present | | | 24 |

[a] On hydrolysis 2–12% appeared in phosphite fraction.

Other workers confirmed that part of the radiophosphorus from neutron-irradiated orthophosphate was not in the original form, although the amount of non-orthophosphate phosphorus varied from case to case. Attempts were made to elucidate the composition of the non-orthophosphate fraction by the addition of a number of anions of phosphorus oxy-acids followed by careful chemical separations. The various forms of phosphorus observed are shown in Table V.
The chemical forms in which the radiophosphorus was found when other phosphorus compounds were irradiated are given in Table VI.

### CAUSES OF DISCREPANCIES

The very large discrepancies among the results obtained by different workers and the wide variation from sample to sample can be attributed to a number of factors. Fiskell[24] showed that phosphates and phosphites interact under certain conditions to give hypophosphates, and other pitfalls in the accepted analytical procedures have been pointed out.[21] Moreover, the target materials have not always been pure,[23] carriers were added for only a few of the possible products, and variations in the irradiation conditions (which were not clearly stated in most cases) could have a profound influence on the results obtained. Table VII shows the effect of temperature and neutron flux on the form of radiophosphorus produced by the irradiation of a variety of substances.[22]

*Table VII.—Percentage of Activity as Non-orthophosphate* $^{32}P$ *for Various Irradiation Conditions*

| Irradiation conditions | *A* | *B* | *C* |
|---|---|---|---|
| Target material | | | |
| $KH_2PO_4$ | 26·69 | 18·31 | 0·57 |
| Florida land pebble | 48·86 | 48·28 | 31·01 |
| Curacao rock | 52·51 | 46·33 | 30·33 |
| Hydroxylapatite | 40·46 | 37·65 | 37·46 |
| Morocco rock | 41·27 | 29·52 | 18·83 |
| Steamed bone | 36·42 | 31·51 | 31·04 |
| Fluorapatite | 37·73 | 34·59 | 26·72 |
| Tricalcium phosphate | 48·45 | 51·78 | 42·79 |
| Phosphate glass | 33·49 | 37·97 | 31·33 |

*A* Low neutron flux, low temperature, irradiation period 4 weeks.
*B* High neutron flux, intermediate temperature, irradiation period 11 days.
*C* High neutron flux, high temperature, irradiation period 4 weeks.

The use of paper electrochromatography for the separation of the various species present in the irradiated compounds led to the production of much more reliable data on the composition of the irradiated material, although the interpretation of these data is still a matter on which there is a wide diversity of opinion. Sato, Strain and their co-workers carried out an extensive investigation using this technique. In earlier work they detected the presence of phosphites in a number of irradiated phosphates,[25] and also observed that condensed phosphates, such as trimetaphosphate and tripolyphosphate, could be formed either by neutron or gamma irradiation or by heating of phosphates.[26] However, in all cases they found the major constituent to be the unchanged phosphate. Sellers, Sato, and Strain showed by chemical analysis that the products of neutron-plus-gamma irradiation are essentially the same as those arising from gamma irradiation alone when the irradiations are carried out in a vacuum (Table VIII).[27]

Electrochromatographic analysis showed that for the neutron-plus-gamma irradiation of $Na_2HPO_4$ the distribution of $^{32}P$ is similar to that of the inactive isotope, a

Table VIII.—*Irradiation Products of Phosphorus Compounds*

| Compound | Irradiation | Products found by direct chemical determination (mole per cent) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_3PO_4$ | $H_3PO_3$ | $H_3PO_2$ | $H_4P_2O_7$ | $PH_3$ | $H_2$ |
| $Na_2HPO_4$ | *A* | 100 | Not detected | Not detected | Not detected | Not detected | Trace |
| | *B* | 100 | Not detected | Not detected | Not detected | Not detected | Trace |
| $Na_2HPO_3$ | *A* | 2·5 | 89·0 | 4·0 | Not detected | Not detected | $1{\cdot}4 \times 10^{-4}$ |
| | *B* | 2·0 | 92·0 | 4·0 | Not detected | Not detected | $1{\cdot}6 \times 10^{-4}$ |
| $NaH_2PO_2$ | *A* | 2·0 | 20·0 | 62·0 | Not detected | Not detected | $3{\cdot}8 \times 10^{-3}$ |
| | *B* | 0·4 | 9·0 | 80·0 | Not detected | Not detected | $1{\cdot}1 \times 10^{-3}$ |
| $PH_3$ | *A** | — | — | — | — | 56·4 | 43·6 |
| | *B* | — | — | — | — | 94·9 | 5·1 |

*A* Neutron flux $10^{13}$ n.cm$^{-2}$sec$^{-1}$, time of irradiation 2 days, $\gamma$ dose $1{\cdot}5 \times 10^9$ r.
*B* Neutron flux aero, time of irradiation 7 days, $\gamma$ dose $3 \times 10^8$ r.
* A small amount of red radiactive solid was also formed.

very small amount appearing in non-orthophosphate forms, but this was not so for the irradiation of $Na_2HPO_3$ and $NaH_2PO_2$. Moreover, for these two compounds the electrochromatograms formed from neutron-irradiated targets differed considerably from those formed from γ-irradiated targets and subsequently neutron activated. Pairs of electrochromatograms for $Na_2HPO_3$ and $NaH_2PO_2$ are shown superimposed in Figs. 1 and 2. From these results it is clear that while the observed distri-

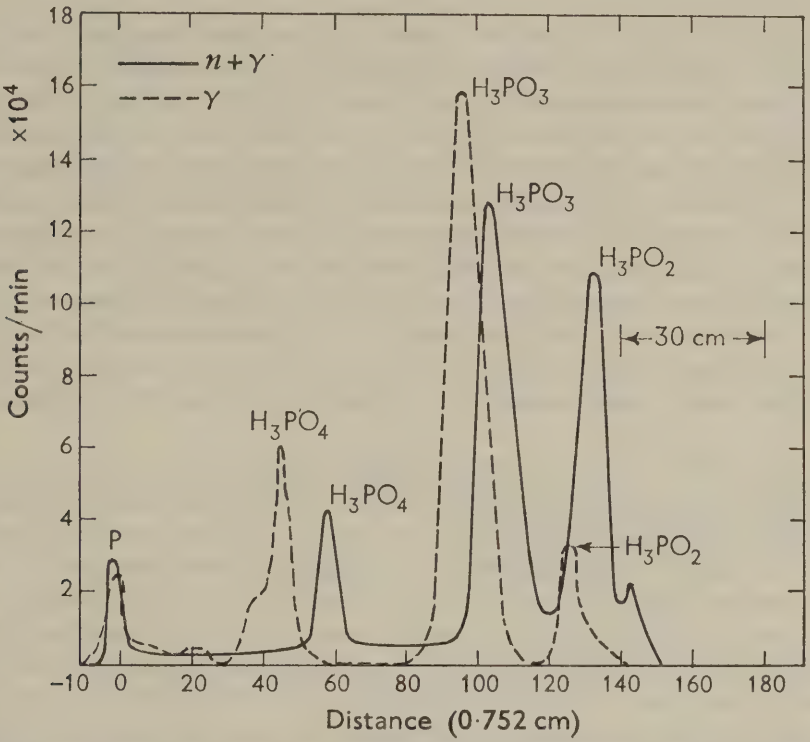

FIG. 1.—Comparison of radioactive products formed by gamma and by neutron-plus-gamma irradiation of $Na_2HPO_3$

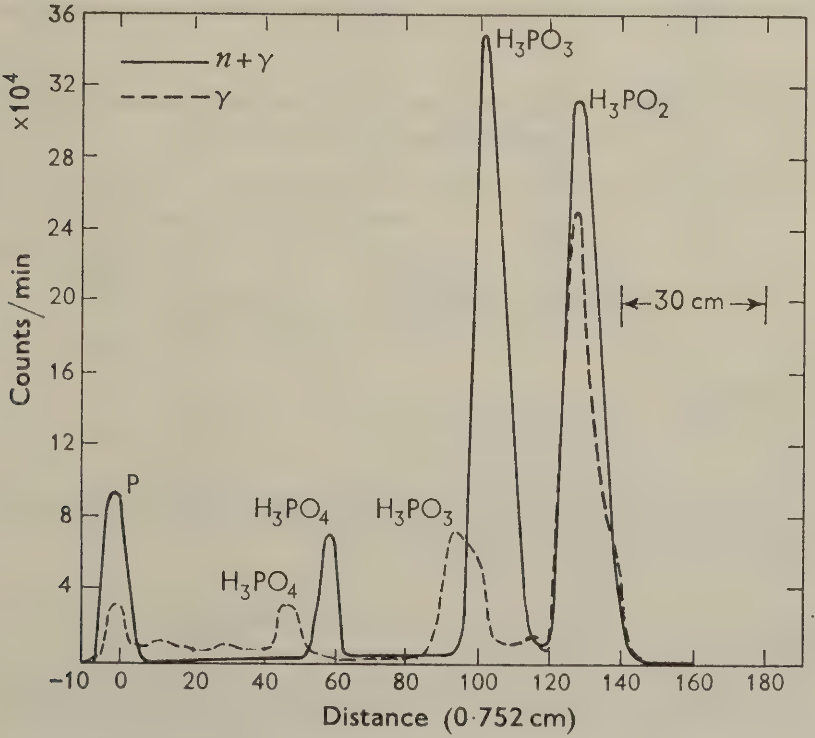

FIG. 2.—Comparison of radioactive products formed by gamma and by neutron-plus-gamma irradiation of $NaH_2PO_2$

bution of $^{32}P$ in irradiated orthophosphate could have arisen solely as a result of the effect of the high $\gamma$-ray flux, the active isotope being formed by neutron capture unaccompanied by chemical change, there must have been a large chemical effect brought about by neutrons in irradiated phosphite and hypophosphite.

### EFFECT OF TEMPERATURE

The fact that very little of the $^{32}P$ formed on neutron irradiation of disodium hydrogen phosphate appeared in non-orthophosphate form led these authors to suggest that the disruption of chemical bonds takes place to a much smaller extent than had been suggested by earlier workers, and to attribute the much lower retention previously observed to the combined effects of neutrons, gamma rays and air. Later, however, they discovered that the temperature of the specimens during irradiation had been 155°C. instead of 40°–50°C. as a result of the action of pile radiation on the quartz containers used, which contained boron as an impurity.[28-9] It had already been shown that thermal annealing can reduce the amounts of non-orthophosphate $^{32}P$ present,[21] and Table IX gives the results of an investigation[30] in which elution from an anion exchange column was used to separate the constituents of irradiated $KH_2PO_4$.[31] The Table shows clearly the change in composition brought about by annealing.

In view of the possible effects of thermal annealing in their previous work, Sato, Sellers and Strain carried out further experiments in which the temperature of the irradiated specimen was kept below 30°C. by the use of pure quartz containers and a lower neutron flux.[29] They irradiated in a vacuum a large number of orthophosphates and condensed phosphates, and in all cases found that the major part of the $^{32}P$ produced was in the form of the starting material. In the irradiated orthophosphates small amounts of other forms of phosphorus were found. These included a trace of material, probably elemental phosphorus, which did not migrate under the conditions of electrochromatography employed, and a small amount of unidentified material which did not correspond with any of the well-known phosphorus compounds; this form of phosphorus was most noticeable in the irradiated monobasic and dibasic sodium, potassium, and ammonium salts. Irradiation of pyrophosphate and trimetaphosphate produced traces of phosphate and of an unidentified product.

*Table IX.—Effect of Thermal Annealing on the Chemical Form of $^{32}P$ in Neutron-irradiated* $KH_2PO_4$ [30]

| | Percentage of $^{32}P$ found as | | | | |
|---|---|---|---|---|---|
| | Ortho-phosphate | Pyro-phosphate | Tri-phosphate | Fraction *A* | Fraction *B* |
| After irradiation | 69 | 3·4 | 14·9 | 8·0 | 4·6 |
| After irradiation and annealing at 175°C. for 24 hr. | 96·3 | 0·2 | 1·1 | 1·2 | 0·4 |

Fractions *A* and *B* were identified, but did not include phosphite, hypophosphite, tetraphosphate, trimetaphosphate and tetrametaphosphate.

In other experiments[28, 32] the effect of a high irradiation temperature on $Na_2HPO_4$ was studied. The temperatures attained by neutron irradiation of the containers were 155°C. for quartz, 368°C. for 'boron-free' glass, and 537°C. for lime glass; slightly lower temperatures were reached with samples in the containers. Samples of $Na_2HPO_4$ irradiated in 'boron-free' or lime glass were almost completely converted to pyrophosphate.

In a discussion of these results, the view is expressed that the $^{32}P$ atoms formed in irradiated phosphates are in general unable to escape from the cages of oxygen atoms which form their immediate environment. This view is based on the electronic bond structure of the phosphate group, and the chemical changes accompanying the irradiation of phosphites and hypophosphites are attributed to their having a less compact cage structure. Recent work by Yoshihara and Yokoshima,[34] in which samples were irradiated in air at temperatures below 50°C. and then subjected to paper chromatography, gave results strikingly different from those obtained by Sato. In Table X are given the chemical forms of $^{32}P$ observed in these experiments. The values quoted are those first obtained after the irradiation; in some cases the values showed a gradual change with time while in others the values fluctuated by a few per cent. With the hydrated salts there seemed to be a slow conversion of phosphite or hypophosphite to phosphate on standing for a few days, attributed to an oxidation process. In irradiated $Na_2HPO_4,12H_2O$ and $Na_4P_2O_7,10H_2O$ no phosphite could be detected, but some of the pyrophosphate present was gradually converted to phosphate. The absence of phosphite in these two cases is rather surprising in view of the large amount found in irradiated $Na_3PO_4,12H_2O$.

*Table X.—Chemical Forms of* $^{32}P$ *in Neutron-irradiated Phosphates and Phosphite*

| Target | Percentage of $^{32}P$ found as | | | |
|---|---|---|---|---|
| | Phosphate | Phosphite and hypophosphite | Pyrophosphate | Higher polyphosphates |
| $H_3PO_4$ | 89·2 | 5·1 | 2·5 | 2·0 |
| $KH_2PO_4$ | 43·5 | 13·9 | 11·8 | 29·5 |
| $NH_4H_2PO_4$ sample I | 47·8 | 13·1 | 8·4 | 29·3 |
| $NH_4H_2PO_4$ sample II | 54·1 | 7·1 | 18·1 | 19·7 |
| $NaH_2PO_4,2H_2O$ | 78·2 | 2·4 | 16·8 | 2·4 |
| $NaH_2PO_4,H_2O$ | 78·6 | 4·7 | 8·6 | 7·9 |
| $NaH_2PO_4$ | 21·2 | 17·3 | 25·9 | 34·9 |
| $(NH_4)_2HPO_4$ | 34·2 | 22·6 | 13·3 | 24·8 |
| $Na_2HPO_4,12H_2O$ | 70·3 | — | 28·1 | 1·5 |
| $Na_2HPO_4$ | 24·3 | 20·2 | 16·5 | 37·5 |
| $Na_3PO_4,12H_2O$ | 45·8 | 47·3 | 6·7* | |
| $Na_3PO_4$ | 20·7 | 24·2 | 18·3 | 35·1 |
| $Zn_3(PO_4)_2$ | 29·6 | 36·2 | 9·3 | 24·8 |
| $Na_4P_2O_7,10H_2O$ | 47·9 | — | 45·3 | 7·1 |
| $Na_4P_2O_7$ | 9·4 | 24·8 | 36·2 | 26·5 |
| $Na_2HPO_4,5H_2O$ | 4·5 | 77·2 | 9·6 | 7·6 |

* Pyrophosphate and higher polyphosphates.

The results of an investigation by Lindner and Harbottle[35, 9] present an even more striking contrast to those of Sato. Essentially the same technique of paper electrochromatography was used, but the samples were usually irradiated at dry ice temperature for only half an hour and stored in dry ice before analysis. Under these conditions the retention of $^{32}P$ as orthophosphate was often as low as 10%, as shown in Table XI. Preliminary experiments showed that at dry-ice temperature it made very little difference whether the irradiation was carried out in air or in a vacuum, and the results given in Table XI show that the products from anhydrous compounds are not significantly affected by preliminary drying of the samples. It was also shown that the amount of radioactive orthophosphate formed in the irradiation of $Na_2HPO_4,2H_2O$, which was about 16% at this temperature, is increased to 37% when the irradiation is carried out with no cooling in the same position in the reactor. The effect of thermal annealing is shown in Table XII, from which it can be seen that there is a general increase in the yield of orthophosphate on annealing at 30°C. for about 4 days.

From these results it is concluded that bond rupture occurs in a very large proportion of the activated phosphate groups, giving rise to a considerable range of products, and that thermal annealing, which is a fairly rapid process at higher temperatures, occurs at an appreciable rate at room temperature. This picture fits reasonably well with the results obtained by earlier workers and by Yoshihara,[34] but does not seem to account for the very high retention of orthophosphate observed by Sato[29] at 30°C. However, in Sato's experiments the irradiation period was five days, and it is shown by Lindner that extensive annealing can occur during such an irradiation, even with a moderate neutron and gamma flux.

### EFFECT OF HYDRATION

The effect of 'dilution' of the phosphate groups by crystal water can be clearly seen from Table XI. Condensed compounds containing more than two phosphorus atoms per molecule are not readily formed when the phosphate groups in the target are separated by water molecules, so that in the hydrated target materials the yields of tripolyphosphate are lower and the yields of orthophosphate higher than in the anhydrous compounds, whilst the yields of pyrophosphate are more or less constant. The yields of the unknown species C change in much the same way as those of tripolyphosphate, and it therefore seems likely that C has two or more phosphorus atoms per molecule. The *iso*hypophosphate formed in these irradiations was found

*Table XI.—Distribution of Recoil Species in Irradiated Orthophosphates*

| Target | Pre-treatment | Percentage of $^{32}$P found as | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *A* | *B* | *C* | *D* | *E* | *F* | *G* | *H* | *I* | *J* |
| $K_3PO_4$ anh. | | 5·7 | 11·1 | 7·9 | 24·4 | 7·0 | 18·9 | 6·8 | 11·5 | 6·7 | |
| † | *a* | 4·7 | 7·7 | 8·8 | 20·8 | 5·9 | 17·9 | 16·1 | 11·4 | 6·0 | 0·8 |
| $K_2HPO_4$ anh. | *e* | 7·8 | 9·0 | 13·1 | 26·5 | 2·0 | 9·6 | 9·2 | 11·8 | 8·2 | 2·8 |
| | *f* | 7·5 | 11·0 | 13·6 | 26·5 | 3·4 | 9·3 | 9·6 | 9·5 | 6·3 | 2·8 |
| | *b* | 7·7 | 10·3 | 14·9 | 27·1 | 1·8 | 9·5 | 10·0 | 9·9 | 6·4 | 2·4 |
| $KH_2PO_4$ | | 13·4 | 15·8 | 13·4 | 21·6 | 1·0 | 10·9 | 2·8 | 11·4 | 8·0 | 1·7 |
| $(NH_4)_3PO_4,3H_2O$ | | | | | | | 19·0 | 3·5 | 23·4 | 15·4 | 1·9 |
| $(NH_4)_2HPO_4$ anh. | | 6·6 | 12·1 | 9·7 | 17·0 | 1·2 | 10·2 | 4·5 | 16·4 | 18·6 | 3·6 |
| $(NH_4)H_2PO_4$ anh. | | 11·2 | 16·3 | 15·4 | 17·3 | 1·0 | 9·6 | 2·7 | 14·2 | 8·4 | 4·3 |
| $Li_3PO_4$ anh. | *b* | 15·5 | 4·7 | 7·4 | 22·9 | 2·8 | 29·5 | 7·9 | 5·4 | 3·3 | |
| | *a* | 14·7 | 4·0 | 7·5 | 20·3 | 2·9 | 30·3 | 10·3 | 5·2 | 3·2 | |
| | *c* | 14·8 | 7·6 | 8·4 | 15·5 | | 33·6* | 10·0 | 5·3 | 3·2 | 1·3 |
| $Na_3PO_4,12H_2O$† | | 0·5 | 13·0 | 1·2 | 9·3 | 2·2 | 38·1 | 2·0 | 22·7 | 10·3 | 0·8 |
| $Na_2HPO_4$ anh. | | 10·5 | 10·6 | 12·9 | 25·5 | 2·4 | 9·7 | 9·9 | 10·1 | 10·4 | |
| | *d* | 12·2 | 11·7 | 12·0 | 27·1 | 2·8 | 9·3 | 8·6 | 8·2 | 6·8 | 1·0 |
| $Na_2HPO_4,2H_2O$ | | 5·3 | 16·6 | 3·9 | 22·8 | 1·1 | 16·2 | 4·9 | 13·2 | 14·7 | 1·3 |
| $Na_2HPO_4,7H_2O$† | | 1·3 | 17·9 | 1·6 | 15·3 | 1·1 | 31·5 | 3·2 | 15·7 | 11·3 | 1·1 |
| $Na_2HPO_4,12H_2O$† | | 1·3 | 11·4 | 0·9 | 11·9 | 2·5 | 31·9 | 3·0 | 21·9 | 12·5 | 2·1 |
| $NaH_2PO_4$ anh. | | 11·1 | 13·5 | 9·2 | 24·3 | 1·0 | 9·9 | 6·3 | 12·4 | 10·6 | 1·7 |
| $NaH_2PO_4,H_2O$† | | 8·7 | 13·9 | 8·0 | 19·1 | 1·6 | 17·9 | 5·2 | 15·7 | 7·9 | 2·1 |
| $NaH_2PO_4,2H_2O$ | | 13·0 | 21·0 | 5·4 | 14·1 | 0·7 | 23·1 | 2·2 | 12·5 | 6·6 | 1·0 |
| $NaH_5(PO_4)_2,H_2O$ | | 15·6 | 15·6 | 8·3 | 18·7 | 0·8 | 14·3 | 4·1 | 13·6 | 6·0 | 3·9 |

*A* Tripolyphosphate.
*B* Pyrophosphate.
*C* Unknown, probably two species.
*D* Isohypophosphate.
*E* Hypophosphate.
*F* Orthophosphate.
*G* Diphosphate (and possibly another species).
*H* Phosphite.
*I* Hypophosphite.
*J* Other unidentified species.

*a* Vac. dried at 105°C.
*b* Vac. dried at room temperature.
*c* Dried at 110°C.
*d* Dried for ½ hr. at 110°C.
*e* Dried for ½ hr. at 135°C.
*f* Dried with conc. $H_2SO_4$.
* Fractions *E* and *F* combined.
† Mean of two sets of results.

*Table XII.—Effect of Annealing on the Chemical Form of Neutron-irradiated Orthophosphates*[9]

| Target | Temp. of anneal. | Change in percentage of $^{32}P$ found as | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *A* | *B* | *C* | *D* | *E* | *F* | *G* | *H* | *I* | *J* |
| $Li_3PO_4$ anh. | 30°C. | −5·7 | +3·2 | | −6·6 | −2·0 | +7·3 | +3·6 | | | |
| $Na_2HPO_4,7H_2O$ | 30°C. | | −4·5 | −1·4 | −12·4 | +0·8 | +26·3 | −2·1 | +4·5 | −8·5 | −1·6 |
| $K_3PO_4$ anh. | 30°C. | +2·1 | | | −7·8 | +3·2 | +2·4 | −1·0 | +5·6 | −2·0 | |
| $K_2HPO_4$ anh. | 30°C. | +0·4 | −4·9 | −5·0 | −12·0 | +3·0 | +13·2 | −6·1 | +15·2 | +0·5 | −0·9 |
| $(NH_4)_2HPO_4$ anh. | 30°C. | −2·5 | −0·7 | | −10·5 | | | −3·4 | +27·1 | −7·4 | |
| $Na_2HPO_4,2H_2O$ | room temp. | −1·5 | −1·0 | +0·4 | −5·2 | | +7·7 | −2·1 | +5·1 | −5·5 | −0·7 |

*A* Tripolyphosphate.
*B* Pyrophosphate.
*C* Unknown, probably two species.
*D* Isohypophosphate.
*E* Hypophosphate.
*F* Orthophosphate.
*G* Diphosphite (and possibly another species).
*H* Phosphite.
*I* Hypophosphite.
*J* Other unidentified species.

to be specifically labelled in the trivalent part of the molecule; this implies that whilst the activated phosphorus atom may appear in a reduced state there is no appreciable effect of the phosphorus recoil on the oxidation state of the phosphate group to which it becomes attached. This is also borne out by the absence of pyrophosphate from the observed products. It is concluded that at the sites in the lattice where the recoiling $^{32}$P atoms are trapped little disorder is produced and there is little fragmentation.

A number of other phosphorus compounds were studied briefly in the course of this investigation, and gave a range of recoil products different from that observed for orthophosphates. The results are summarized in Table XIII, in which all unidentified products are combined although a number of separate peaks were observed.

*Table XIII.—Distribution of Recoil Species in Irradiated Non-orthophosphates*[9]

| Target | Percentage of $^{32}$P found as | | | | | | |
|---|---|---|---|---|---|---|---|
| | *A* | *B* | *C* | *D* | *E* | *F* | *G* |
| $Na_2HPO_3,5H_2O$ | 3·8 | 5·3 | 4·5 | 3·7 | 34·4 | 23·6 | 24·7 |
| $NaH_2PO_2,H_2O$ | 1·5 | 2·5 | 2·4 | 6·8 | 22·4 | 42·1(b) | 22·2 |
| $Na_4P_2O_7$ anh. | 32·5 | 11·9 | 1·6 | 8·2 | 12·2 | 4·6 | 28·7 |
| $Na_4P_2O_7,10H_2O$ | 4·4 | 6·3 | | 29·2(a) | 28·4 | 11·7 | 20·0 |
| $Na_2H_2P_2O_7$ anh. | 6·2 | 20·9 | 3·6 | 3·6 | 21·1 | 7·7 | 32·1 |
| $Na_2H_2P_2O_6,6H_2O$ | 4·7 | 2·3 | 4·9 | 10·4 | 28·0 | 24·7 | 29·7 |

*A* Pyrophosphate.
*B* Probably isohypophosphate.
*C* Hypophosphate.
*D* Orthophosphate.
*E* Phosphite.
*F* Hypophosphite.
*G* Unidentified species.

(a) Fractions *C* and *D* combined.
(b) Includes an unidentified species.

EFFECT OF ANNEALING

The effects of annealing irradiated ammonium and potassium dihydrogen phosphates under a variety of conditions have been studied by Claridge and Maddock.[36–7] In contrast to Lindner's results[35] they found a threshold for thermal annealing at 40 to 50°C., but as their irradiations were carried out at reactor temperature some annealing must have occurred at this stage, resulting in the removal of all fragments capable of undergoing recombination at this temperature. They observed two parameters of the phosphates before and after annealing; these were 'orthophosphate retention' and 'total phosphate retention', the difference between them being attributable to fragments which yield, for example, hypophosphate or pyrophosphate on solution. On thermal annealing at temperatures below 100°C. the orthophosphate retention was found to increase rapidly at first, but at a later stage the rate of increase fell to a fairly constant value of about $\frac{1}{2}$% per hour. The total phosphate retention showed little change until the whole of the phosphate had been converted to orthophosphate, the effect of annealing being the formation of fragments which give rise to orthophosphate on solution, from fragments which give rise to other anions containing pentavalent phosphorus atoms. There is little contribution to orthophosphate formation from reduced phosphorus species at these temperatures, but at temperatures above 100°C. the orthophosphate and 'total phosphate' retention rise together, and the process must be either

reduced phosphorus fragments → orthophosphate fragments

or

reduced phosphorus fragments → 'polyphosphate'
→ orthophosphate fragments

Annealing with ultra-violet light or with 1·8 Mev. electrons brought about some change in the orthophosphate retention, but the effect on the total phosphate retention was much more pronounced, and the kinetic curves obtained indicate a first-order recombination process in the early stages, followed by a slower process of uncertain kinetics. Although the orthophosphate retention is only slightly increased by photon annealing, both the rate and extent of the increase on subsequent thermal annealing are found to have been enhanced, the degree of enhancement being related to the increase in total phosphate retention which had occurred during the photon annealing process. The effect of annealing by electrons is similar, but in this case there is a significant change of orthophosphate retention during the radiation annealing process as well as during the subsequent thermal annealing. Radiation annealing therefore seems to operate mainly by converting reduced phosphorus fragments to potential 'polyphosphate' fragments, the increase in orthophosphate retention on electron annealing being possibly attributable to local thermal effects of the radiation.

Some further experiments on the thermal annealing of irradiated phosphates have been briefly described.[38] On annealing of irradiated $Na_3PO_4$ at 167°C. a rapid increase in the amount of orthophosphate occurs, the proportion of $^{32}P$ found in this form changing from 30% to 70% in about an hour; in the subsequent slow stage the proportion of orthophosphate reaches about 85% in the course of 24 hr. The initial stage of the annealing of irradiated $Na_2HPO_4$ resembles that for $Na_3PO_4$, but is followed by a fairly rapid conversion of orthophosphate to pyrophosphate and other polyphosphates. In both cases the increase of orthophosphate content in the early part of the anneal is presumably due to the conversion of polyphosphate fragments to fragments which form orthophosphate in solution, as there is very little decrease in the amounts of reduced phosphorus species formed, but the behaviour of $Na_2HPO_4$ during the later stages is surprising. Annealing of irradiated sodium pyrophosphate was found to result in an increase in the pyrophosphate content at the expense of other polyphosphates.

### IRRADIATION OF PHOSPHORUS TRICHLORIDE

Apart from the studies of salts of phosphorus oxy-acids there has been little work on the effects of neutron irradiation on inorganic phosphorus compounds. Some work on phosphine[27] has already been mentioned, and the effect of irradiation of phosphorus trichloride has been studied by Hein and his co-workers.[39-40] In the course of their earlier work[39] they found that for irradiation periods of 19 hr. to 3 weeks and for temperatures of 30°–140°C. the amount of $^{32}P$ retained as $PCl_3$ is more or less constant, the mean value being 88%. The chemical state of the remaining 12% of the radiophosphorus is not very clear: 1–2% was found on distillation in the same fraction as $PSCl_3$, but it was thought unlikely that it could be in this form, a further 5% was sometimes found as $POCl_3$, and there was always a little $^{32}P$ left in the residue of high boiling-point components at the end of a distillation. Although in this irradiation $^{32}P$ can be produced by the $^{35}Cl(n, \alpha)^{32}P$ reaction, this process would contribute only about 1% of the total $^{32}P$, so that it cannot account for that part of the radiophosphorus not in the form of $PCl_3$.

In later work[40] shorter irradiation times were used, and lower values for the retention were observed, the lowest being 62%; extrapolation to zero irradiation period indicated that 50 to 60% of the radiophosphorus would remain as $PCl_3$ under these conditions. The composition of the remainder of the active material was very uncertain; a very small amount was found to distil with $PSCl_3$, and when lightly irradiated samples were distilled at atmospheric pressure a fraction of high specific activity distilled at the end of the $PCl_3$ fraction, but the rest of the activity remained in the distillation flask. The possibility of the presence of $P_2Cl_4$ was considered, as this might decompose to $PCl_3$ and give rise to the high specific activity fraction, but no firm conclusion could be reached. Irradiation by $\gamma$-rays produced a marked increase in the yield of $^{32}P$ as $PCl_3$, and it was thought that this accounted for the results

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obtained in the longer neutron irradiations where up to 95% retention was observed. Some of the results of this work are given in Tables XIV and XV.

In an investigation by Henglein[40a] a value of about 65% was obtained for the retention in irradiated solutions of $PCl_3$ in carbon tetrachloride, but a marked fall of the retention was found when hydrogen-containing solvents were used (Fig. 3).

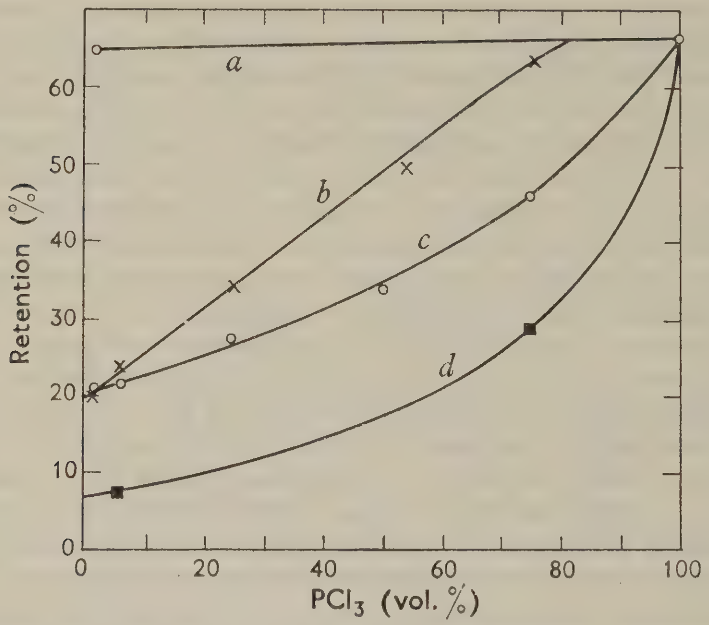


FIG. 3.—Retention of $^{32}PCl_3$ in organic solutions solvent: *a* carbon tetrachloride
*b* benzene
*c* *cyclo*hexane
*d* *cyclo*hexene

This effect was attributed to the removal of chlorine atoms formed by the disruption of the $PCl_3$ molecule, and from the fact that the change in retention with increase in solvent concentration was gradual it was concluded that the reactions leading to

*Table XIV.—Distribution of $^{32}P$ in Neutron-irradiated Phosphorus Trichloride*[40]

| Specific activity[(a)] (atoms of $^{32}P$ per ml.) | Percentage of $^{32}P$ found | | | |
|---|---|---|---|---|
| | as $PCl_3$[(b)] | in $PSCl_3$ fraction | in peak[(c)] | in residue not distilled |
| $7{\cdot}58\times10^{8}$ | 62·2±2 | | 0 | 29·0 |
| $1{\cdot}21\times10^{9}$ | 67·2±3 | 1·0 | 7 | 19·4 |
| $5{\cdot}95\times10^{9}$ | 73·6±3 | 0·9 | [(d)] | 13·0 |
| $8{\cdot}25\times10^{9}$ | 69·4±3 | 0·7 | 16 | 14·4 |
| $8{\cdot}25\times10^{9}$ | 65·5 | | 0 | 28·8 |
| $8{\cdot}51\times10^{9}$ | 98·0±2 | 0·0 | 0 | 0·67 |
| $9{\cdot}44\times10^{9}$ | 62·4±2 | 1·0 | 17 | 12·7 |
| $9{\cdot}72\times10^{9}$ | 75·0±2 | 0·7 | 2 | 14·2 |
| $1{\cdot}98\times10^{10}$ | 79·7±5 | 1·0 | 0 | 11·4 |
| $7{\cdot}99\times10^{10}$ | 94·1±4 | 0·4 | 0 | 1·0 |
| $1{\cdot}57\times10^{11}$ | 95·4±2 | 0·8 | 0 | 2·0 |
| $2{\cdot}29\times10^{11}$ | 87·3±2 | 2·0 | 0 | 3·1 |

(a) Specific activity is taken as a measure of total neutron dose.
(b) Excluding activity in 'peak'.
(c) High specific activity fraction distilling at the end of $PCl_3$ fractions.
(d) Some activity present but not determined.

retention must occur in the neighbourhood of the track of the recoiling phosphorus atom.

Preliminary work on the irradiation of $POCl_3$ indicated that a variety of products was formed.[40] These were mainly $^{32}PCl_3$ and $^{32}POCl_3$, but there appeared to be a trace of $^{32}PSCl_3$ and there was a considerable unidentified residue. A more detailed study[40b] revealed that the proportions of the various products formed were markedly dependent on the time of irradiation and on the conditions of irradiation and dissolution, as shown in Table XV. The fraction identified as 'high-boiling component' was thought to be $^{32}PCl_5$, but this could not be proved and the evidence was conflicting.

It was concluded that the chief primary product was $^{32}PCl_3$, and that conversion to other species during the irradiation resulted from radiation-induced exchange reactions. This view is supported by the effect of subsequent $\gamma$-irradiation, and by the effect of small amounts of carrier $PCl_3$ in maintaining a high yield of $^{32}PCl_3$. (The amounts of carrier used were such that there was only a small contribution to the $^{32}P$ activity from activation of the carrier.) No significant exchange between $PCl_3$ and $POCl_3$ could be detected in experiments conducted in the absence of radiation. The high-boiling component, which appears to be produced from $^{32}PCl_3$ under the influence of radiation, is itself converted to $^{32}POCl_3$ as irradiation proceeds, so that the final product is almost entirely $^{32}POCl_3$.

*Table XV.—Distribution of* $^{32}P$ *in Neutron-irradiated Phosphorus Oxychloride*

| Irradiation time | Percentage of $^{32}P$ found | | | |
|---|---|---|---|---|
| | as $PCl_3$ | as $POCl_3$ | in high-boiling component | Notes |
| 30 sec. | 22·5 | 45 | 25 | *ab* |
| 30 sec. | 57 | 30 | 6 | |
| 1 min. | 52 | 35·5 | 32 | *a* |
| 3 min. | 43 | 43 | 9 | |
| 4 min. | 18 | 46 | 31 | |
| 5 min. | 10 | 57 | 25·5 | *a* |
| 10 min. | 12·5 | 58·5 | 27·5 | *a* |
| 20 min. | 8·5 | 56 | 36 | *a* |
| 1 hr. | 6 | 84 | 6 | |
| 24 hr. | 4 | 84 | 7 | |
| 30 sec. | 1 | 35 | 61 | *c* |
| 1 min. | 80 | 11 | 5 | *d* |
| 4 min. | 80 | 15 | 2 | *d* |

*a* Mean values from two experiments.
*b* Hydrolysis thought to have occurred during distillation.
*c* Irradiated with $2{\cdot}4 \times 10^7$ r. $\gamma$ after neutron irradiation.
*d* Carrier $PCl_3$ present during irradiation.

## Irradiation of Organic Phosphorus Compounds

Although the chemical state of radiophosphorus has not been studied as extensively in neutron-irradiated organophosphorus compounds as in inorganic compounds of phosphorus, the first investigation was carried out as long ago as 1937 when it was found that 40% of the activity produced by the irradiation of triphenyl phosphate in benzene could be extracted by water, presumably in ionic form.[41] It was also observed that the active material could be adsorbed by carbon, and carrier-free material could be produced by either method. Very little attention was given to this subject, however, until 20 years later, although in the search for methods of production of carrier-free $^{32}P$ it was observed that extraction of radiophosphorus with water from solutions of irradiated triphenylphosphine gave yields of about 50% with benzene as the solvent[42] but of only 3% with xylene as the solvent.[43] In the latter case it was suggested that the reason for the very low yield might be exchange between the radioactive phosphorus atoms and the inactive phosphorus atoms of the triphenylphosphine, but the discrepancy between the behaviour in the two different solvents has not been satisfactorily explained. More recent work[44] has shown that only 2–3% of the total activity remains as triphenylphosphine when the irradiation is carried out in vacuum, and that about half of the activity is found as triphenylphosphine oxide, diphenylphosphinic acid, benzenephosphonic acid, benzenephosphinic acid, phosphorous acid, and phosphoric acid. As in the early experiments on inorganic phosphorus compounds the identification of the products in this case was unsatisfactory as carriers were added only for species thought to be possible, and in fact about half of the total activity remained unidentified.

About 85% of the radioactive phosphorus in irradiated triphenylphosphine oxide can be extracted with water from a solution in chloroform, and about 70% can be co-precipitated with ferric hydroxide from alcoholic solution. Under these conditions all the triphenylphosphine oxide remains in the organic solvent.[45]

### IRRADIATION OF TRIMETHYLPHOSPHINE

The active volatile products of the irradiation of trimethylphosphine have been separated by gas chromatography,[44, 46] and their yields are given in Table XVI. In each experiment the remainder of the activity was found on the walls of the irradiation ampoule. It can be seen that the fraction of the radiophosphorus retained as trimethylphosphine is very small and decreases as the pressure of the target compound is reduced. Dilution of the target material with argon resulted in a reduction of the yields of all volatile products, and it was therefore concluded that bond rupture occurred in most if not all recoils, the residual $(CH_3)_3{}^{32}P$ being formed by recombination. On the other hand dilution with krypton gave rise to an increase in the yields of di- and tri-methylphosphines so that the results are not fully consistent with this explanation. In some cases the active deposit on the ampoule walls (amounting in some cases to over 99% of the total activity) was examined by electrochromatography, and it was established that the activity was not due to orthophosphate or phosphite.[44a]

### IRRADIATION OF BUTYL PHOSPHATES

A number of investigations have been carried out into the chemical state of radiophosphorus in neutron-irradiated tributyl phosphate (TBP). The amount of carrier-free $^{32}P$ which can be extracted into an aqueous phase varies with the pH,[47] reaching a maximum of 54·3% for potassium hydroxide solution of pH 12·5. Campbell, Poczynajlo, and Siuda[48] examined the active irradiation products by the addition of carriers followed by solvent extraction and conventional chemical separations. As in other studies where this technique is used there is the possibility of unknown or unidentified products appearing in some of the fractions obtained, and this has been indicated in Table XVI. It can be seen that the amounts of radiophosphorus retained as TBP increase with the severity of the irradiation conditions, and must therefore be mostly attributed to recombination of fragments produced during the recoil process, the primary retention being not greater than 5 or 6%. It is suggested that the recombination process involves organic radicals formed by the irradiation. The dibutyl phosphate (DBP) fraction is little affected by a change of irradiation conditions, most of the recombination taking place at the expense of monobutyl phosphate (MBP) and inorganic phosphorus compounds, but it must be borne in mind that the DBP and MBP fractions probably contain other unknown products. Most of the inorganic phosphorus is found in the form of orthophosphate and orthophosphite, the contribution from other oxyacids and phosphine being very small.

The effect of the conditions of the irradiation has been more fully studied.[49] A thermal neutron flux of $2{\cdot}6 \times 10^{11}$ neutrons cm.$^{-2}$ sec.$^{-1}$, and gamma and fast neutron doses of about $10^4$ to $10^5$ rads were used, so that considerable recombination

*Table XVI.—Chemical Forms of* $^{32}$P *in Neutron-irradiated Trimethylphosphine*[44, 46]

| Expt. no. | Thermal flux (n. cm.$^{-2}$ sec.$^{-1}$) | Cd ratio | Target composition (mm. Hg) | | | Irradiation period (hr.) | Percentage of $^{32}$P found as | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $(CH_3)_3P$ | Ar | Kr | | $PH_3$ | $CH_3PH_2$ | $(CH_3)_2PH$ | $(CH_3)_3P$ |
| 1 | $5{\cdot}7 \times 10^8$ | 4,000 | 155 | | | 12 | 48·5 | 3·5 | | 1·4 |
| 2 | $2{\cdot}7 \times 10^9$ | 120 | 155 | | | 20 | 15·4 | 3·0 | 0·4 | 2·4 |
| 3 | $2{\cdot}7 \times 10^9$ | 120 | 100 | | | 24 | 13·7 | 4·9 | 0·8 | 2·8 |
| 4 | $2{\cdot}7 \times 10^9$ | 120 | 11 | | | 24 | 11·8 | 5·9 | 0·2 | 0·6 |
| 5 | $5{\cdot}2 \times 10^{12}$ | 40 | 155 | | | 3 | 3·9 | 0·8 | 0·3 | 3·8 |
| 6 | $7 \times 10^{12}$ | 40 | 1·8 | | | 1 | 3·1 | 2·2 | 0·3 | 0·4 |
| 7 | $7 \times 10^{12}$ | 40 | 1·1 | 50 | | 1 | 0·3 | 0·3 | 0·1 | 0·1 |
| 8 | $7 \times 10^{12}$ | 40 | 1·3 | 50 | | 1 | 0·00 | 0·02 | 0·02 | 0·04 |
| 9 | $7 \times 10^{12}$ | 40 | 1·8 | | 38 | 1 | 1·5 | 1·8 | 1·3 | 4·7 |

*Table XVII.—Distribution of* $^{32}$P *in Irradiated Tributyl Phosphate*[48]

| Neutron flux (n. cm.$^{-2}$ sec.$^{-1}$) | Irradiation period (hr.) | Percentage of $^{32}$P found as | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *A* | *B* | *C* | *D* | *E* | *F* | *G* | *H* | *I* | *J* | *K* | *L* |
| low$^{(a)}$ | $^{(b)}$ | | 5·3 | | 22·2 | 35·8 | 36·6 | | | | | | |
| low$^{(a)}$ | $^{(b)}$ | | 5·0 | | 25·9 | 33·5 | 35·5 | | | | | | |
| $10^9$ | 144 | ⩽0·01 | 5·5$^{(c)}$ | 93·9$^{(c)}$ | 28·4$^{(c)}$ | 31·6$^{(c)}$ | 30·2$^{(c)}$ | 13·6$^{(d)}$ | 1·9$^{(c)}$ | | 3·8$^{(c)}$ | ⩽2 | 13·0$^{(c)}$ |
| $10^9$ | 144 | | 5·4$^{(c)}$ | 92·0$^{(c)}$ | | 64·8$^{(c)}$ | 26·5$^{(c)}$ | 13·3$^{(d)}$ | 1·1$^{(c)}$ | 1·1$^{(c)}$ | 2·8$^{(c)}$ | ⩽2 | 11·8$^{(c)}$ |
| $9 \times 10^{10}$ | 6 | ⩽0·001 | 31·0 | | 27·0 | 25·7 | 14·4 | 6·2 | | | 0·0 | | 9·1$^{(c)}$ |
| $9 \times 10^{10}$ | 6 | | 31·0 | | 27·4 | 25·7 | 14·4 | 5·3 | | | 0·0 | | 9·1 |
| $9 \times 10^{10}$ | 6 | | 27·6 | | 28·4 | 25·7 | 14·8 | 4·5 | | | 0·0 | | 10·3 |
| $9 \times 10^{10}$ | 6 | | 27·7 | | 28·4 | 25·4 | 15·7 | 4·6 | | | 0·0 | | 11·2 |
| $9 \times 10^{11}$ | 48 | ⩽0·0001 | 68·0 | | 21·0 | 6·7 | 2·8 | 0·4 | | | 0·2 | | 2·2 |
| $9 \times 10^{11}$ | 48 | | 67·8 | | 21·1 | 6·7 | 2·8 | 0·5 | | | 0·1 | | 2·2 |
| $9 \times 10^{11}$ | 48 | | 59·0 | | 24·0 | 11·4 | 3·2 | 1·1 | | | 0·0 | | 2·1 |
| $9 \times 10^{11}$ | 48 | | 59·1 | | 24·1 | 11·7 | 3·1 | 1·4 | | | 0·0 | | 2·0 |

*A* Phosphine.
*B* TBP (and possibly other compounds remaining in TBP after extraction with NaOH).
*C* All compounds in NaOH extract.
*D* DBP (and possibly other compounds extracted from NaOH fraction by benzene).
*E* MBP plus a small proportion of inorganic P acids (and any other compounds extracted from NaOH fraction by amyl alcohol).
*F* Inorganic phosphorus acids (aqueous solution after benzene and amyl alcohol extractions).
*G* Orthophosphate.
*H* Hexametaphosphate.
*I* Hypophosphate and pyrophosphate.
*J* Pyrophosphate, metaphosphate, and hypophosphate.
*K* Hypophosphite (and possibly phosphorus).
*L* Orthophosphite.
(a) Irradiated with Ra–Be source.
(b) Irradiation period not stated.
(c) Mean of two or more determinations.
(d) Mean of analyses by three methods.

would be expected from the results given in Table XVII. The results of these experiments, presented in Table XVIII, show this to be the case, but the introduction of scavengers leads to a distribution of products similar to that previously obtained at a low neutron flux; dilution of the target TBP does not further reduce the yield of active TBP. From the effects of scavengers and of dilution, and from the distribution of irradiation products of mono- and di-butyl phosphates in the presence of air as a scavenger (Table XIX), responsibility for the yields of the various organic products can be apportioned to various types of process as shown in Table XX. The basis for this apportionment is that thermal reactions are eliminated by scavengers, which

*Table XVIII.—Effect of Irradiation Conditions on the Chemical Forms of* $^{32}$P *in Neutron-irradiated Tributyl Phosphate*[49]

| Scavenger | Solvent | TBP concentration (mole fraction) | Percentage of $^{32}$P found as | | | |
|---|---|---|---|---|---|---|
| | | | TBP | DBP | MBP | Inorganic phosphorus |
| — | | | 21 ± 2 | 27 ± 2 | 30 ± 1 | 19 ± 2 |
| Air | | | 6·5 ± 0·3 | 29 ± 2 | 34 ± 2 | 26 ± 0·4 |
| Air(a) | | | 11·2 ± 0·5 | 37·1 ± 0·7 | 28·4 ± 0·5 | 19 ± 1 |
| Oxygen | | | 5·9 ± 0·3 | 28 ± 2 | 30 ± 1 | 31 ± 1 |
| $I_2$(b) | | | 5·0 ± 0·3 | 19·2 ± 0·2 | 41 ± 2 | 30·2 ± 0·8 |
| Air + $I_2$ | | | 6·0 ± 0·2 | 25 ± 2 | 38 ± 3 | 27 ± 1 |
| | *n*-Heptane | 0·1 | 7 ± 2 | 46 ± 2 | 26 ± 1 | 16 ± 3 |
| | *n*-Heptane | 0·01 | 8·7 ± 0·7 | 44 ± 1 | 34·8 ± 0·4 | 10 ± 1 |
| | Benzene | 0·1 | 7·1 ± 0·1 | 14 ± 1 | 40 ± 1 | 34 ± 1 |
| | Benzene | 0·01 | 10·2 ± 0·4 | 16 ± 1 | 44·5 ± 0·6 | 25 ± 1 |

(a) Temperature, 80°C. (b) $10^{-2}$ mole fraction.

*Table XIX.—Chemical Forms of* $^{32}$P *in Neutron-irradiated Butyl Phosphates*[49]

| Target | Percentage of $^{32}$P found as | | | |
|---|---|---|---|---|
| | TBP | DBP | MBP | Inorganic phosphorus |
| TBP + air | 6·5 ± 0·3 | 29 ± 2 | 34 ± 2 | 26 ± 0·4 |
| DBP + air | 4 ± 2 | 8 ± 1 | 49 ± 3 | 22 ± 2 |
| MBP + air | 2·5 ± 0·2 | 2·3 ± 0·2 | 26·3 ± 0·6 | 65 ± 1 |

*Table XX.—Mechanism of Formation of Active Products of Neutron-irradiated Tributyl Phosphate*[49]

| Process | Contribution to formation of | | | | | |
|---|---|---|---|---|---|---|
| | TBP | | BDP | | MBP | |
| | *a* | *b* | *a* | *b* | *a* | *b* |
| Bond rupture failure | 4 | 19 | 26 | 96 | 30 | 100 |
| 'Hot' reactions | 2 | 9·5 | | | | |
| Thermal reactions | 15 | 71 | 1 | 4 | 0 | 0 |

*a* Expressed as a percentage of total $^{32}$P activity.
*b* Expressed as a percentage of yield of the product being considered.

remove any radicals formed before they can be reached by a diffusing phosphorus atom, and that dilution of the target material in the presence of scavengers leads to a reduction in the amount of recombination by either thermal or 'hot' reactions; on the other hand only 'hot' reactions can account for the active TBP formed on irradiation of DBP or MBP in the presence of a scavenger. The effect of a change of temperature on the distribution of products is attributed to an increase of the 'hot' reactions at the lower temperature as a result of the lowering of the diffusion coefficients; the excited phosphorus atom is then less likely to escape from its immediate environment of organic radicals. It can be seen that primary retention (one or more P-organic bonds remaining intact) and 'hot' reactions contribute very little to TBP formation but are entirely responsible for MBP formation. Most of the active TBP is produced after the primary event by reactions occurring outside the nest of radicals formed in the neighbourhood of the recoiling atom.

## THE CHEMICAL STATE OF $^{32}$P PRODUCED BY THE $^{32}$S($n, p$)$^{32}$P REACTION

The atoms of $^{32}$P produced by irradiation of sulphur are subject not only to 'hot' atom reactions, but also to the chemical effects resulting from their presence in trace quantities in solution or in a foreign crystal lattice. Moreover, the recoil energies of the $^{32}$P atoms are very much higher in these circumstances than they are for the $n, \gamma$ reaction. The earliest observations on the chemical state of the radiophosphorus produced from sulphur were made during investigations of possible processes for its production in a carrier-free condition. It was noticed that all the radiophosphorus formed by the irradiation of carbon disulphide could be removed from the solution by simultaneous electrolysis with copper electrodes, and was deposited in a form soluble in nitric or hydrochloric acid, but that deposition was incomplete when aluminium electrodes were used and did not occur at all on platinum electrodes.[50-1] The radiophosphorus produced by the irradiation of carbon disulphide could be adsorbed in a water soluble form on red phosphorus, formed during the irradiation from a small amount of white phosphorus dissolved in the carbon disulphide.[52] Aten[53-4] determined the distribution of radiophosphorus between phosphate and phosphite (or hypophosphite) for a number of target materials, but the use of very few carriers severely restricted the number of products which could be observed; the results obtained are given in Table XXI. Whitmore[55] observed that most of the radiophosphorus formed in sodium sulphide and thiourea gave rise to oxyanions on solution, but that a considerable part of that formed in sulphur or carbon disulphide was in the form of elemental phosphorus. No attempt was made, however, to study the products in further detail.

*Table XXI.—Chemical Form of Radiophosphorus in Neutron-irradiated Sulphur Compounds*[54]

| Target | Percentage of radiophosphorus found as | |
|---|---|---|
| | Phosphate | Phosphite and hypophosphite |
| $K_2SO_4$ | 90 | 10 |
| $Na_2SO_4,10H_2O$ | 98 | 2 |
| $Na_2SO_3,7H_2O$ | 50; 44 | 50; 56 |
| $Na_2S$ hydrate* | | 64 to 93 |

* This result indicates that there is much more of the reduced forms of phosphorus than of phosphate, but does not take into account other possible forms.

Nilsson[56] found that in irradiated sulphur containing a small proportion of amorphous sulphur (S$\mu$), insoluble in carbon disulphide, a considerable part of the radiophosphorus is associated with the amorphous sulphur, although only a small

*Table XXII.—Forms of Radiophosphorus in Irradiated Sulphur*[56]

| Form of sulphur target | Distance from centre of reactor* (cm.) | Percentage of $S\mu$ in irradiated target | Percentage of activity carried by $S\mu$ | | | Percentage of activity extracted by water from | | | | Percentage of aqueous extract as pentavalent | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $^{35}S$ | $^{32}P$ | $^{33}P$ | $^{32}P$ | | $^{33}P$ | | $^{32}P$ | | $^{33}P$ | |
| | | | | | | *a* | *b* | *a* | *b* | *a* | *b* | *a* | *b* |
| Sublimed | 48 | 0·08 | 0·4 | 30 | — | — | — | — | — | — | — | — | — |
| | 60 | 0·08 | 0·3 | 32 | — | 37 | 35 | — | — | 84 | 90 | — | — |
| | 124 | 0·09 | 0·04 | 62 | 59 | — | — | — | — | — | — | — | — |
| | 150 | 0·09 | 0·4 | 60 | 71 | 32 | 42 | 24 | 24 | 88 | 85 | 84 | 80 |
| Crystallized | 48 | 0·02 | 0·2 | 19 | — | 51 | 40 | — | — | 82 | 91 | — | — |
| | 138 | 0·02 | 0·01 | 14 | 13 | 26 | 40 | 19 | 34 | 75 | 82 | 82 | 87 |

*a* In nitrogen.
*b* In air.
* The ratio of thermal to fast neutron flux was much higher in the reflector (radius over 100 cm.) than in the reactor core.

proportion of the $^{35}S$ produced is found in the insoluble material (Table XXII). The addition of various phosphorus compounds or of more S$\mu$ to the carbon disulphide solution had in most cases very little effect on the distribution of radiophosphorus, although the amount of radiophosphorus in the S$\mu$ phase varied with the amount of S$\mu$ present at the end of the irradiation. It was therefore concluded that adsorption on the S$\mu$ did not afford a complete explanation of the phenomenon, and at least part of the effect was attributed to the formation of S$\mu$ in the 'displacement spikes' produced by the recoiling phosphorus atoms; the recoiling $^{35}S$ atoms have much lower energy and it was assumed that they would be unable to cause the formation of stable aggregates of S$\mu$. It was also shown that annealing of S$\mu$ to S$\alpha$ could occur during irradiation (Table XXIII) and it was calculated that this would account for that part of the radiophosphorus not associated with S$\mu$. An attempt was made to study the chemical state of the radiophosphorus in the soluble part of the sulphur target, but very few carriers were used and only pentavalent phosphorus was identified. In Table XXII are shown the amounts of radiophosphorus which could be extracted from the carbon disulphide solutions by water containing small amounts of phosphoric, phosphorous, and sulphuric acids as carriers, and the amounts of pentavalent phosphorus in these extracts.

A method has been developed for the separation of radiophosphorus from neutron-irradiated sulphur by extraction with water at the transition point from the rhombic to the monoclinic form.[57] It was found that the yields increased markedly with increasing porosity and decreasing particle size; the diffusion of phosphorus out of the sulphur particles must therefore be slow. The small amount of phosphorus not extracted by water could be extracted by benzene, and was thought to be probably in elemental form. The chemical form of the radiophosphorus extracted by water has been examined by Dahl and Birkelund.[58-9] Solutions were examined for a wide range of phosphorus compounds, but most of the phosphorus was found to be present as orthophosphate (Table XXIV). A more detailed examination of the radiophosphorus present at various stages of the process was carried out by means of two-directional paper chromatography. A preliminary washing of the irradiated sulphur

*Table XXIII.—Effect of Irradiation on* S$\mu$ *Content of Sulphur*[56]

| Form of sulphur target | Sublimed | Crystallized |
|---|---|---|
| Percentage of S$\mu$ before irradiation | 0·47 | 0·02 |
| Percentage of S$\mu$ after irradiation | 0·08 to 0·09 | 0·02 |

*Table XXIV.—Chemical Forms of* $^{32}P$ *Extracted by Water from Irradiated Sulphur*[58]

| Solution | Percentage of $^{32}P$ found as* | | |
|---|---|---|---|
| | Orthophosphoric acid | Orthophosphoric acid bound to impurities | Pyrophosphoric acid |
| *A* | 99·5 ± 0·2 | 0·14 ± 0·06 | 0·36 ± 0·16 |
| *B* | 98·5 ± 0·3 | 0·14 ± 0·08 | 1·35 ± 0·23 |

*A* After extraction with water.
*B* After evaporation of solution *A*.
* The following species were not found in significant quantities: $PH_3$, P, $H_3PO_2$, $H_3PO_3$, $H_4P_2O_6$, $(HPO_3)_3$, higher polyphosphates.

yielded a mixture of small quantities of ortho-, pyro-, tri-, tetra-, and tetrametaphosphates, together with other long-chain polyphosphates. At the beginning of the extraction process about 70% of the radiophosphorus was in the form of orthophosphate, the remainder being present as polyphosphates which were hydrolyzed to orthophosphate during the extraction, so that at the end of the extraction process about 98% of the phosphorus-32 was in the form of orthophosphate; the residual amounts of pyrophosphate and other polyphosphates were attributed to the interaction of processes of adsorption and desorption with formation at hot spots on the glassware and hydrolysis in the solution.

The chemical state of radiophosphorus in irradiated sulphates has been studied by Fomin and Maslova,[60] who examined the distribution among phosphate, phosphite, and hypophosphite. The results obtained are given in Table XXV. The three forms of phosphorus investigated appear to have been formed in roughly equal amounts in solutions containing carriers, but most of the radiophosphorus appeared as phosphate in the absence of carriers. The difference in behaviour was attributed to oxidation of tracer amounts of the lower valency forms, probably by dissolved oxygen, or by the products of radiolysis of water, but this oxidation process does not appear to be very important in irradiated sulphuric acid. In irradiated crystalline sulphates there was

*Table XXV.—Distribution of* $^{32}$P *in Irradiated Sulphates between Phosphate, Phosphite and Hypophosphite*[60]

| Target material | Condition during irradiation or dissolution | Percentage of $^{32}$P found as(a) | | |
|---|---|---|---|---|
| | | Phosphate | Phosphite | Hypophosphite |
| $H_2SO_4$(1:2) | carrier-free | 31–34 | 36–39 | 30–31 |
| $H_2SO_4$(1:2) | with carriers | 25–28 | 28–47 | 24–38 |
| $K_2SO_4$(soln.) | carrier-free | 80 | 15 | 5 |
| $K_2SO_4$(soln.) | with carriers | 31–35 | 27–32 | 32–36 |
| $K_2SO_4$(soln.) | with carriers(b) | 22–34 | 39–56 | 22–31 |
| $Na_2SO_4$(soln.) | carrier-free | 61–64 | 20–21 | 16–20 |
| $Na_2SO_4$(anh.) | carrier-free | 85–91 | 5–11 | 0–9 |
| $Na_2SO_4$(anh.) | with carriers | 70 | 8 | 22 |
| $K_2SO_4$(cryst.) | with carriers | 92–94 | 4 | 2–4 |

(a) Values given in this table are in most cases extreme values obtained from several irradiations or from several analyses of the solution from one irradiation.
(b) KOH added to give hydroxyl ion concentration of 0·35–0·54 mole/l.

*Table XXVI.—Chemical Form of* $^{32}$P *in Irradiated Sulphur Compounds*

| Target | Treatment or form of target | Percentage of $^{32}$P in valency states below +5 |
|---|---|---|
| $Na_2SO_4$ | Dried in air | 16 |
| $Na_2SO_4$ | ,, | 23 |
| $Na_2SO_4,10H_2O$ | ,, | 0 |
| $Na_2S_2O_3,5H_2O$ | ,, | 45 |
| $Na_2SO_3,7H_2O$ | ,, | 61 |
| KCNS | ,, | 61 |
| $Na_2SO_4$ | Fused before irradiation | 5 |
| $Na_2SO_4$ | Roasted after irradiation | 8 |
| $Na_2SO_4,10H_2O$ | Fused after irradiation | 0 |
| $Na_2S_2O_3,5H_2O$ | Dried at 100°C. after irradiation | 5 |
| $Na_2SO_3,7H_2O$ | Dried at 150°C. after irradiation | 52 |
| KCNS | Solution (56 g. per 100 ml. water) | 44 |
| $H_2SO_4$ | 92·7% | 45 |

*Table XXVII.—Chemical Form of $^{32}$P in Irradiated Sulphates*

| Nature of solvent | Percentage of $^{32}$P in valency states other than +5 | | | | | | |
|---|---|---|---|---|---|---|---|
| | Non-reducing | | | Reducing | | | |
| | Acid | Neutral | Alkaline | Acid | Neutral | Alkaline | |
| Target | | | | | | | Remarks |
| $Li_2SO_4$ | 3·1 | 4·9–6·2 | 4·0 | | 6·9 | | |
| $Li_2SO_4,H_2O$ | 18·7 | 18·6–29·9 | 19·0 | | 19·6–34·3 | | |
| | | 27·8 | | | 31·0 | | Dehydrated after irr. anh. |
| | | 25·5–28·3 | | | 31·0 | | hydrated before irr. |
| | | 24·0–26·3 | | | | | 'internal' irradiation 5·4–6·8% in +1 state. |
| $Li_2SO_4,D_2O$ | | 27·5–29·4 | | | 30·5–31·0 | | |
| $Na_2SO_4$ | 1·4–2·5 | 2·6–3·3 | 1·7–5·9 | 9·0 | 9·6 | 8·3 | |
| $Na_2SO_4,10H_2O$ | 2·8 | 2·8 | 2·8 | 2·5 | | 2·4 | |
| | | 7·0 | | | | | 'Internal' irradiation. |
| $NaHSO_4,0{\cdot}13H_2O$ | 21·3 | 20·7 | 23·8 | | 22·8 | | 9·8–10·0% in +1 state in separate 'internal' irradiations. |
| $NaHSO_4,H_2O$ | 17·4–18·2 | 17·2–18·5 | 17·3–18·9 | | 16·9–18·2 | | |
| | | 25·0 | | | | | 'Internal' irradiation 2·8% in +1 state. |
| $K_2S_2O_7$(fused) | | 12·9 | | | | | 'Internal' irradiation. |
| $K_2SO_4$ | 1·4–2·2 | 2·6–5·7 | 2·3–5·8 | 6·0 | 3·3–6·0 | 6·0 | |
| $KHSO_4$ | 13·4–13·9 | 13·7–15·0 | 15·1–16·5 | | 12·7–14·7 | | |
| | | 18·2 | | | | | 'Internal' irradiation 13·9–14·0% in +1 state. |
| $(NH_4)_2SO_4$ | 23·3–27·0 | 29·0–39·4 | 28·4–40·6 | 24·4–27·6 | 23·5–38·7 | 27·6–42·3 | No phosphine observed. |
| | | 47·6 | | | | | 'Internal' irradiation 17·6–18·0% in +1 state. |
| $NH_4HSO_4$ | 23·5 | 27·2 | 24·9 | | | | |
| | | 29·9 | | | | | 'Internal' irradiation 1·6–4·0% in +1 state. |
| $H_2NNH_2,H_2SO_4$ | 48·2 | 49·8–51·0 | 51·9 | | | | |
| $2NH_2OH,H_2SO_4$ | 18·1 | 18·0 | 17·8 | | | | |
| $MgSO_4$ | 6·6 | 6·1–6·3 | 6·8 | 7·6 | 6·2–9·6 | 6·8 | |
| | 4·4 | 3·8–4·3 | 5·8 | 4·9 | 4·3–4·4 | 4·5 | Hydrated (+7$H_2O$) after irradiation. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $MgSO_4,H_2O$ | 19·2–20·3 | 15·5–5–23·5 | 15·5–22·1 | | 13·3–24·2 | | |
| | | 21·1 | | | | | Hydrated (+6$H_2O$) after irradiation. |
| $MgSO_4,7H_2O$ | 5·8–11·6 | 7·6–12·0 | 5·7–11·8 | | 6·6–14·4 | | |
| | 9·9 | 9·9 | 10·0 | | | | Dehydrated (−6$H_2O$) after irr. at 160°C. for 20 hours. |
| $CaSO_4$ | | 8·8 | | | 8·8 | | |
| $CaSO_4,2H_2O$ | | 35·9 | | | 38·0 | | |
| $FeSO_4,7H_2O$ | | 73·0–75·7 | | | | | 'Internal' irradiation. |
| $FeSO_4,(NH_4)_2SO_4,6H_2O$ | | 68·0 | | | | | 'Internal' irradiation. |
| $CoSO_4,7H_2O$ | | 26·0–28·0 | | | | | 'Internal' irradiation. |
| $NiSO_4,H_2O$ | 24·6 | | | | | | 'Internal' irradiation. |
| | 26·8–32·6 | | | | | | |
| α-$NiSO_4,6H_2O$ | 24·5–32·1 | | | | | | |
| | 37·9–40·5 | | | | | | 'Internal' irradiation 8·9% in +1 state. |
| | 31·6 | | | | | | 'Internal' irradiation sample stored for 20 days 5·7% in +1 state. |
| β-$NiSO_4,6H_2O$ | 35·4–39·2 | | | | | | 'Internal' irradiation. |
| $NiSO_4,7H_2O$ | 36·2 | | | | | | 'Internal' irradiation. |
| $ZnSO_4,H_2O$ | | 27·8 | | | | | 'Internal' irradiation. |
| $ZnSO_4,6H_2O$ | | 12·5 | | | | | 'Internal' irradiation. |
| $ZnSO_4,7H_2O$ | | 5·3 | | | | | |
| | | 14·7 | | | | | 'Internal' irradiation. |

little difference between the distributions with and without carriers, and the predominant formation of phosphate in these cases was attributed to interaction between the 'hot' phosphorus atoms and the oxygen of disrupted sulphate ions. The amounts of phosphorus used as carriers in the irradiations were not large enough for an appreciable contribution to the yield of $^{32}P$ from the $^{31}P(n, \gamma)^{32}P$ reaction.

In another series of investigations[61] it was found that the radiophosphorus formed by the irradiation of sulphur monochloride was in the form of $^{32}PSCl_3$. The amounts of $^{32}P$ in the lower valency states of phosphorus were measured for a number of targets under a variety of conditions (Table XXVI). It can be seen that for sodium sulphate, particularly in the hydrated form, a large proportion of the radiophosphorus was in pentavalent form, but that lower valency states were prevalent for sulphuric acid and for targets containing sulphur in less highly oxidized forms. The results show broad agreement with those obtained by Fomin and Maslova[60] (Table XXV), and Aten[54] (Table XXI).

An extensive investigation of the chemical forms of radiophosphorus in irradiated sulphates, sulphites, and sulphides has been carried out by Lindner.[62] Some of the results of this investigation are summarized in Tables XXVII, XXVIII, and XXIX. The values given in these Tables are generally the extreme values obtained in a series of experiments; most of the irradiations were carried out with stray neutrons from a cyclotron, but a few were carried out at higher dose rates and for shorter times with the neutrons produced by bombardment of a beryllium target. These are indicated in the Tables as 'internal' irradiations.

For most targets the results show a fairly wide scatter, but comparison with the results given in Tables XXI and XXVI shows that there is generally good agreement with the work of other investigators. The most marked feature of Lindner's results is the strong dependence of the chemical state of the radiophosphorus on the presence of hydrogen in the target molecule. Very little non-orthophosphate phosphorus is found in anhydrous non-hydrogenous sulphates and sulphites, but in many cases the amount is increased to 20–40% by the presence of a few molecules of water of crystallization. On the other hand higher hydrates show a wide range of behaviour, amounts of orthophosphate varying from 60 to 95%. Target materials containing

*Table XXVIII.—Chemical Form of* $^{32}P$ *in Irradiated Sulphites*

| | Percentage of $^{32}P$ in valency states other than +5 | | | |
|---|---|---|---|---|
| Nature of solvent | Acid | Neutral | Alkaline | |
| Target | | | | Remarks |
| $Na_2S_2O_5$ | 2·6–7·0 | 3·1–5·5 | 2·8–4·6 | |
| $Na_2SO_3$ | 16·3–20·2 | 14·6–21·1 | 15·1–16·2 | 2·5–5·1% in +1 state. |
| | 12·9–13·8 | 12·2–14·5 | 13·0–15·6 | Hydrated (+7$H_2O$) after irr. |
| $Na_2SO_3,7H_2O$ | 55·0–60·5 | 52·7–58·7 | 52·1–55·6 | 7·4% in +1 state in a separate 'internal' irradiation. |
| | 54·4 | 54·2–54·6 | 54·0 | Dehydrated (−7$H_2O$) after irr. |
| $K_2S_2O_5$ | 10·3 | 11·0 | 10·7 | |
| $K_2SO_3,2H_2O$ | | 25·3 | 27·4 | |
| $(NH_4)_2SO_3,H_2O$ | | 70·0–71·5 | | 'Internal' irradiation 16·2% in +1 state. |
| $NH_4HSO_3$ | | 29·5–32·4 | | 'Internal' irradiation 14·5–15·2% in +1 state. |

hydrogen bound to nitrogen or in acidic form usually give rise to a considerable amount of radiophosphorus in the lower valency states.

The fact that neither the nature of the carrier solution used in dissolving the target nor post-irradiation treatment such as hydration or dehydration appreciably alters the amount of the reduced forms of phosphorus led Lindner to suggest that most of the recoiling $^{32}P$ atoms attain their final valency state very shortly after the nuclear transformation. The enhancement of the yield of non-orthophosphate phosphorus by the presence of hydrogen in the target molecule was attributed to stabilization of the lower valency states in the target crystal, since P–H bonds are present in phosphite and hypophosphite anions but not in orthophosphate anions. There is, however, a noticeable absence of phosphine in the products of irradiation of sulphates, sulphites, and, surprisingly, the sulphides of sodium and potassium (Table XXIX). On the other hand a considerable fraction of the radiophosphorus in irradiated calcium sulphide is found as phosphine. It was suggested that the absence of phosphine could in many cases be attributed to a preferential formation of P–O bonds, but this cannot be so in the case of potassium sulphide, and the difference in stability between the phosphides of potassium and calcium was invoked to explain the striking differences between the irradiation products of potassium and calcium sulphides.

It was observed that the amount of non-orthophosphate phosphorus in irradiated anhydrous sulphates was reduced considerably if they were heated for a short time in the acid or alkaline carrier solution, but only a very small reduction occurred when a neutral solvent was used. This effect was attributed to the presence of phosphorus compounds (probably thiophosphates) which were not precipitated with the orthophosphate fraction but could be hydrolyzed to give orthophosphate. It is evident from the results of this examination of a large range of sulphur compounds that the final state of the radiophosphorus is in general only slightly influenced by the valency state of the sulphur atoms in the target, and depends largely on other factors such as the presence of hydrogen or oxygen in the molecule.

*Table XXIX.—Chemical Form of* $^{32}P$ *in Irradiated Sulphides*

| Target | $Na_2S,9H_2O$ | $K_2S$ | $K_2S$ | CaS | CaS |
|---|---|---|---|---|---|
| Percentage of $^{32}P$ in valency states | other than $+5^{(a)}$ | other than $+5^{(a)}$ | $+5$ | $+1$ and $+3$ | $-3$ |
| Nature of solvent | | | | | |
| Non-reducing acid | 21·3–34·5 | 8·0–11·2 | | | |
| Non-reducing neutral | 23·4 | 5·7–6·9 | 45·1–59·5 | 11·5–17·8 | 24·9–38·5<br>$21·6^{(b)}$<br>$25·0–47·1^{(c)}$ |
| Non-reducing alkaline | 39·5 | | | | |
| Reducing acid | 27·4–32·9 | | | | |
| Reducing neutral | 19·9 | | | | |
| Reducing alkaline | 34·2 | | | | |

(a) No phosphine observed.
(b) Stored for 2 weeks.
(c) Calculated from activity balance.

Some experiments were carried out at liquid air temperature and the products annealed for various times, and these led to the conclusion that some annealing could occur at room temperature. Variations in the extent of annealing could account for much of the scatter observed in the experiments carried out at ambient temperature.

Irradiation of some targets in the form of solutions showed that in these circumstances the presence in solution of reducing species could exert some influence on the state of the radiophosphorus. The results are given in Table XXX.

More recently Lindner[76] has studied the distribution of $^{32}P$ among the valency states +5, +3, and +1, for fast neutron irradiation at −30°C. The results so far obtained, which are given in Table XXX, are however, only of a preliminary nature, and are subject to modification in the light of future work.

Adams and Campbell[62a] have studied the effect of irradiation of sulphur compounds with pile neutrons. For sodium sulphate and sulphite the results obtained were in general agreement with those obtained by Lindner,[62] but as the experiments were carried out at about 40°C. some annealing is likely to have occurred, and storage of irradiated samples at room temperature resulted in little change of valency state of the radiophosphorus. The fraction of $^{32}P$ in the pentavalent state was found to increase with the irradiation dose, indicating that there was considerable annealing

*Table XXX.—Chemical Form of* $^{32}P$ *in Irradiated Sulphates and Sodium Sulphite*

| Target compound | Percentage of $^{32}P$ in valency states | | |
|---|---|---|---|
| | +5 | +3 | +1 |
| $(NH_4)_2SO_4$ | 47·0 | 28·8 | 24·2 |
| $(NH_4)_2SO_4$ (dried at 100°C.) | 40·5 | 23·1 | 36·4 |
| $(NH_4)_2SO_4$ (dried in desiccator) | 43·9 | 17·7 | 38·4 |
| $Li_2SO_4,H_2O$ | 64·9 | 25·8 | 9·3 |
| $Li_2SO_4,H_2O$ (vapour phase hydrated) | 62·5 | 26·5 | 11·0 |
| $Li_2SO_4,D_2O$ ( ,, ,, ,, ) | 62·6 | 26·0 | 11·4 |
| $Na_2SO_4,10H_2O$ | 92·7 | 4·9 | 2·4 |
| $NaHSO_4,H_2O$ | 59·0 | 30·8 | 10·2 |
| $Na_2SO_3,7H_2O$ | 36·4 | 52·5 | 11·1 |
| $KHSO_4$ | 69·5 | 21·3 | 9·2 |
| $MgSO_4,H_2O$ | 67·2 | 23·8 | 9·0 |
| $MgSO_4,7H_2O$ | 68·3 | 21·9 | 9·8 |
| $CaSO_4,2H_2O$ | 61·6 | 30·0 | 8·4 |
| $Cr_2(SO_4)_3,15H_2O$ | 53·2 | 39·1 | 7·7 |
| $CrK(SO_4)_2,12H_2O$ | 69·2 | 25·0 | 5·8 |
| $MnSO_4,H_2O$ | 69·8 | 27·2 | 3·0 |
| $FeSO_4,7H_2O$ | 23·4 | 49·6 | 27·0 |
| $FeSO_4,(NH_4)_2SO_4,6H_2O$ | 29·9 | 49·9 | 20·2 |
| $Fe_2(SO_4)_3,6H_2O$ | 83·9 | 12·9 | 3·2 |
| $Fe(NH_4)(SO_4)_2,12H_2O$ | 94·5 | 1·2 | 4·3 |
| $CoSO_4,7H_2O$ | 52·3 | 35·2 | 12·5 |
| $CoSO_4,K_2SO_4,6H_2O$ | 50·4 | 37·4 | 12·2 |
| $CoSO_4,(NH_4)_2SO_4,6H_2O$ | 37·2 | 38·6 | 24·2 |
| $NiSO_4,H_2O$ | 66·0 | 24·7 | 9·3 |
| $NiSO_4,6H_2O$ | 52·7 | 36·2 | 11·1 |
| $NiSO_4,6H_2O$* | 53·4 | 36·4 | 10·2 |
| $NiSO_4,7H_2O$ | 51·6 | 34·9 | 13·5 |
| $CuSO_4,5H_2O$ | 73·2 | 20·1 | 6·7 |
| $ZnSO_4,7H_2O$ | 78·0 | 15·2 | 6·8 |

* $NiSO_4,7H_2O$ partially dehydrated.

by $\gamma$-radiation. Degassing of potassium thiocyanate crystals before irradiation resulted in a decrease in the amount of pentavalent $^{32}P$, presumably by preventing oxidation of the recoiling fragments by occluded oxygen, although the slight increase in the amount of pentavalent $^{32}P$ resulting from degassing of thiosulphate and sulphite targets does not seem to be consistent with this explanation. Thermal annealing curves for irradiated sulphite and thiocyanate targets showed fast and slow stages similar to those observed for irradiated phosphates,[36–7] indicating that the initial recoil energy has little effect on the subsequent annealing behaviour. The formation of $^{32}P^{5+}$ during the fast stage took place almost entirely at the expense of $^{32}P^{3+}$, and this stage of annealing was thought to be due to the presence of defects or radicals produced in the region near the end of the recoil track.

*Table XXXI.—Chemical Form of* $^{32}P$ *in Irradiated Solutions of Sulphur Compounds*

| Target | $Na_2SO_4$ | $(NH_4)_2SO_4$ | $Na_2SO_3$ | $H_2SO_4$ | $H_2SO_4$ |
|---|---|---|---|---|---|
| Concentration (%) | 10 | 10 | 10 | dil | 96 |
| Percentage of non-orthophosphate $^{32}P$ | 54·2 | 58·2 | 89·5 | 75·2 | 37·8 |

The irradiation of solutions of carbon disulphide in organic solvents leads to the formation of a number of organophosphorus compounds,[63] details of which are given in Table XXXII. The range of products identified in this investigation was limited by the small number of different carriers used, and the investigators considered that the relatively high yield of triphenylphosphine observed could be attributed to the extraction by benzene, in the course of the separation procedure, of species for which no carriers had been added, and which followed the triphenylphosphine carrier. It was pointed out that the observed products could not be primary products, which might well be species such as $C_6H_5PH_2$ or $C_6H_5PCl_2$, and it was concluded that the mechanism of the primary process leading to the formation of di- and tri-phenyl phosphorus compounds was different from that giving rise to monophenyl compounds. The variation of the yield of monophenylphosphonic acid with the proportions of carbon disulphide and organic solvent in the irradiated mixture is shown in Table XXXIII; the difference in yields for the two solvents was attributed to the greater mass of the chlorobenzene molecule and to the presence in this molecule of an atom of mass close to that of the recoiling phosphorus atom.

*Table XXXII.—Chemical Forms of* $^{32}P$ *Produced by Irradiation of Carbon Disulphide in Benzene or Chlorobenzene*[63]

| Mixture | Concn. of $CS_2$ (mole fraction) | Percentage of $^{32}P$ found as | | | |
|---|---|---|---|---|---|
| | | Phosphate | Phenyl-phosphonic acid | Diphenyl-phosphinic acid | Triphenyl-phosphine |
| $CS_2$–$C_6H_6$ | 0·65 | 73·2 | 24·2 | 0·81 | 1·78 |
| | | 72·0 | 26·9 | 0·46 | 0·61 |
| $CS_2$–$C_6H_5Cl$ | 0·68 | 71·0 | 27·2 | 0·22 | 1·56 |
| | | 66·4 | 32·1 | 0·34 | 1·16 |

*Table XXXIII.—Effect of Composition of Target Solution on Yield of* $^{32}$P *as Phenylphosphonic Acid*[63]

| | Carbon disulphide in benzene | | | | | |
|---|---|---|---|---|---|---|
| Mole fraction of $C_6H_6$ | 0·206 | 0·348 | 0·404 | 0·514 | 0·602 | 0·773 |
| Yield of $C_6H_5PO(OH)_2$ (%) | 20·7 | 25·6* | 32·4 | 29·4 | 31·5 | 32·2 |
| | Carbon disulphide in chlorobenzene | | | | | |
| Mole fraction of $C_6H_5Cl$ | 0·145 | 0·322 | 0·372 | 0·426 | 0·542 | 0·748 |
| Yield of $C_6H_5PO(OH)_2$ (%) | 22·4 | 29·7* | 29·6 | 39·7 | 37·1 | 44·8 |

* Mean value from Table XXXII.

## CHEMICAL STATE OF $^{32}$P PRODUCED BY THE $^{35}$Cl($n$, α)$^{32}$P REACTION

The studies which have been carried out on radiophosphorus produced by neutron bombardment of chlorine compounds fall into two broad categories—studies of the valency states of the phosphorus atoms and studies of their diffusion behaviour—and these will be considered separately.

### Irradiation of Inorganic Chlorides

Aten[54] separated the irradiation products of a number of inorganic chlorine compounds into phosphate and phosphite plus hypophosphite fractions, and similar work has been carried out by Korshunov.[61] The results are given in Table XXXIV, from which it can be seen that the amount of pentavalent phosphorus is increased by the presence of water crystallization and is highest for salts containing chlorine in high oxidation states. The difference between the values for magnesium chloride in solution and in the hydrated crystalline form is one for which there does not appear to be a satisfactory explanation.

*Table XXXIV.—The Chemical State of* $^{32}$P *in Irradiated Inorganic Chlorides*

| Target | Form or treatment of target | Percentage of $^{32}$P in valency states below +5[61] or in phosphite plus hypophosphite fraction[54] | Reference |
|---|---|---|---|
| $KClO_4$ | | 1 | 54 |
| $KClO_3$ | | 0 | 54 |
| $MgCl_2$ hydrate | | 7 | 54 |
| $MgCl_2$ hydrate | Dissolved in sulphite solution | 2 | 54 |
| $MgCl_2$ | Soln. (17·4 g. per 100 ml water) | 65 | 61 |
| NaCl | | 62 to 69 | 54 |
| $NH_4Cl$ | Dried in air | 68 | 61 |
| $CaCl_2$ | Dried in air | 47 | 61 |
| $CaCl_2,6H_2O$ | Dried in air | 12 | 61 |

Caillat and Süe observed that about half the radiophosphorus produced by the irradiation of crystalline or fused inorganic chlorides is in pentavalent form, and that the presence of water increases the yield of this form.[64] They also showed that annealing of the *F* centres responsible for the coloration of the irradiated crystals results in a lowering of the proportion of $^{32}$P in pentavalent form[65]; they attributed this to the effect of electrons liberated from the *F* centres during the annealing process. The results of their experiments are summarized in Table XXXV.

*Table XXXV.—Valency States of* $^{32}$P *in Irradiated Inorganic Chlorides*[64–5]

| Target | Form of target | Percentage of $^{32}$P observed(a) | |
|---|---|---|---|
| | | In +5 state | In lower than +5 state |
| LiCl | Fused salt | 51·5 | 43·3 |
| KCl | Fused salt | 49·4 | 50·8 |
| KCl | Satd. soln. | 100 | 0 |
| NaCl | Single crystal | 43 | 57·1 |
| | | 41·5 | 59·6 |
| NaCl | Satd. soln. | 100 | 0 |
| NaCl | Single crystal(b) | 30·5 | 64·7 |

(a) The values given in the table are the mean values from several experiments. For NaCl single crystal they are the mean values from two series of experiments.
(b) Heated to 350°C. for a few minutes after irradiation to remove *F* centres.

It was shown by Carlson and Koski[66] that pre-irradiation treatment of the target, the severity of the irradiation, and exposure to $\gamma$-radiation could all affect the distribution of radiophosphorus amongst the possible valency states. Thorough outgassing of potassium chloride crystals before irradiation by pile neutrons led to a reduction of the yield of pentavalent phosphorus from nearly 100% to 88%, and when a lower neutron dose was used (neutrons being obtained by the reaction $2D \rightarrow T + n$) the change was even more pronounced, the yield of pentavalent phosphorus being 89% for untreated crystals and 40% for outgassed ones. The effect of irradiation conditions is shown in Table XXXVI; the pronounced effect of $\gamma$- or *X*-radiation led the authors to suggest that the high yields of pentavalent phosphorus under severe irradiation conditions could be attributed to the action of the high $\gamma$-radiation also present. Surprisingly, no effect was observed on heating the crystals to 850°C. after irradiation, and this is in direct conflict with the observations of Süe and Caillat.[65]

*Table XXXVI.—Effect of Irradiation Conditions on the Valency Distribution of Radiophosphorus in Potassium Chloride*[66]

| Irradiation conditions | Percentage of $^{32}$P found in the valency states | | | |
|---|---|---|---|---|
| | +5 | < +5 | +1 and +3 | −3 |
| *A* | 95·3 | 4·7 | 2·8 | 1·9 |
| *B* | 36 | 64 | 32 | 32 |
| *C* | 18 | 82 | 43 | 39 |
| *D* | 69 | 31 | | |
| *E* | 62 | 38 | | |

*A* $10^{18}$ n. cm$^{-2}$ by pile irradiation.
*B* $\sim 10^{14}$ n. cm$^{-2}$ from $^{9}$Be($\alpha$, *n*)$^{12}$C reaction.
*C* $5 \times 10^{10}$ n. cm$^{-2}$ from $^{3}$H(*d*, *n*)$^{4}$He reaction.
*D* As *B*, followed by $\sim 10^{6}$ roentgens of 100 KeV. *X*-rays.
*E* As *B*, followed by $2{\cdot}5 \times 10^{6}$ roentgens of $^{60}$Co $\gamma$-rays.

However, the effect of the discharge of *F*-centres has been confirmed by Butterworth and Campbell,[66a] who have shown that during thermal annealing of irradiated potassium chloride crystals there is at one stage a decrease in the proportion of $^{32}$P$^{5+}$, producing a hump in the annealing curve. They have also observed that although considerable annealing occurs on heating pile-irradiated potassium chloride crystals, no significant thermal annealing can be produced when the source of neutrons is the D–T reaction. Cífka[66b] has attributed the oxidation process which occurs during annealing to reaction between the $^{32}$P recoils and *V*-centres. During annealing of crystals doped with cadmium or calcium ions an initial reduction stage was observed, but for pure potassium chloride crystals the reduction stage found by Butterworth and Campbell[66a] was not observed. The yield of pentavalent phosphorus was slightly increased when crystals were outgassed before irradiation. The opposite effect had been observed by Carlson and Koski,[66] but in their experiments the proportion of phosphorus in the pentavalent state was much greater, and since the experiments carried out by Cífka were at dry ice temperature it is possible that the high yields obtained by Carlson and Koski resulted from thermal and radiation annealing in which trapped oxygen played some part.

The results of some experiments carried out by Lindner[62] are given in Table XXXVII. Comparison of these results with those given in Tables XXXIV and XXXV shows that very good agreement is obtained for most target materials, the yields of non-orthophosphate phosphorus being very low for oxyanions and hydrated species, and high for anhydrous crystals. An interesting feature is the variation of the yield from potassium chloride with the form of pre-irradiation treatment, recrystallization increasing the yield of the lower valency forms especially when carried out from an aqueous solution saturated with hydrogen. This was attributed by Lindner to the removal of oxidizing impurities from the crystal. No effect was observed when samples of potassium perchlorate were recrystallized before irradiation, so that the presence of oxygen in the crystal lattice clearly outweighs any impurity effect in this case. Irradiation of sodium perchlorate in 10% solution, however, was found to give rise to 53·7% of the radiophosphorus in non-orthophosphate forms. Some further

*Table XXXVII.—Chemical Form of* $^{32}$P *in Irradiated Chlorine Compounds*

| Nature of solvent | Percentage of $^{32}$P in valency states other than +5 | | | | | | |
|---|---|---|---|---|---|---|---|
| | Non-reducing | | | Reducing | | | |
| | Acid | Neutral | Alkaline | Acid | Neutral | Alkaline | |
| Target | | | | | | | Notes |
| NaCl | 66·3–68·2 | 55·5–58·5 | 45·5–51·6 | 62·9 | 71·9 | 68·1 | |
| KCl (sample 1) | 53·5 | 50·1 | 51·5 | | | | |
| KCl (sample 2) | | 19·8–22·7 | | | | | *a* |
| | | 31·2–34·1 | | | | | *b* |
| | | 33·2–34·0 | | | | | *c* |
| | | 42·9–43·0 | | | | | *d* |
| $NH_4Cl$ | 32·8–34·1 | 27·6–30·1 | 27·2–33·1 | 33·1–35·0 | 29·1–31·8 | 27·8–35·0 | *e* |
| $MgCl_2,6H_2O$ | 7·3 | 7·3 | | 6·7–6·8 | 7·4 | | |
| $NaClO_2,H_2O$ | | $\ll 1$ | | | $\ll 1$ | | |
| $KClO_3$ | $\ll 1$ | $\ll 1$ | $\ll 1$ | $\ll 1$ | $\ll 1$ | $\ll 1$ | |
| $NaClO_4,H_2O$ | | 0·8 | | | | | *f* |
| $KClO_4$ | | $\ll 1$ | | | | | |
| $NH_4ClO_4$ | | 0·4–0·5 | | | 0·5 | | |
| $MgClO_4,6H_2O$ | | 3·3 | | | | | |
| | | 3·9–7·6 | | | | | *f* |

*a* No pre-irradiation treatment.
*b* Recrystallized from aqueous solution saturated with nitrogen.
*c* Recrystallized from aqueous solution saturated with oxygen.
*d* Recrystallized from aqueous solution saturated with hydrogen.
*e* 7·5% in −3 state in acid solvent.
7·8% in −3 state in neutral solvent.
*f* 'Internal' irradiation.

*Table XXXVIII.—Chemical Form of* ${}^{32}P$ *in Irradiated Chlorides*

| Target compound | Percentage of ${}^{32}P$ in valency states | | |
|---|---|---|---|
| | +5 | +3 | +1 |
| $MgCl_2,6H_2O$ | 82·1 | 14·1 | 3·8 |
| $CaCl_2,2H_2O$ | 64·9 | 23·5 | 11·6 |
| $CrCl_3,6H_2O$ | 35·1 | 45·4 | 19·5 |
| $MnCl_2,4H_2O$ | 15·0 | 43·8 | 41·2 |
| $FeCl_2,4H_2O$ | 4·4 | 30·0 | 66·4 |
| $FeCl_3,6H_2O$ | 96·9 | 2·1 | 1·0 |
| $CoCl_2,6H_2O$ | 30·7 | 38·8 | 30·5 |
| $CoCl_2,NH_4Cl,4H_2O$ | 23·7 | 35·3 | 41·0 |
| $NiCl_2,6H_2O$ | 47·9 | 35·9 | 16·2 |
| $CuCl_2,2H_2O$ | 65·1 | 29·7 | 5·2 |

results, of a preliminary nature, for the fast neutron irradiation of chlorides at −30°C. are given in Table XXXVIII.

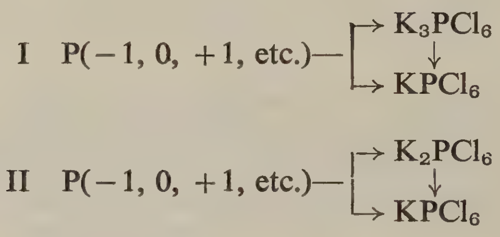
### EFFECT OF ANNEALING

An extensive investigation of the products of irradiation of single crystals of potassium chloride by very high energy protons has recently been carried out[67]; the nuclear reactions which led to the formation of radiophosphorus were ${}_{17}Cl(p, 3p+xn){}^{32}_{15}P$ and ${}_{19}K(p, 5p+xn){}^{32}_{15}P$, and although this section is mainly concerned with $n, \alpha$ reaction it is convenient to consider this spallation reaction at this stage, since the ${}^{32}P$ atoms formed are present as foreign atoms in the potassium chloride lattice. Analyses were carried out for phosphate, phosphite, and hypophosphite, and it was found that 50–60% of the radiophosphorus was in the form of phosphate, but annealing at a high temperature (650°–700°C.) before irradiation reduced this fraction to 10–20%. The crystals used for subsequent experiments were all annealed before irradiation. In one series of experiments phosphine was used as an additional carrier, and an attempt was made to isolate elemental phosphorus, but none could be detected. The results of this series of experiments are given in Table XXXIX. Post-irradiation annealing experiments were carried out at a series of temperatures between 200°C. and 400°C., and these gave results similar to those obtained for the thermal annealing of irradiated phosphates. An initial rapid increase in the phosphate yield was followed by a very slow increase, and at 400°C. the change in phosphate yield took place at the expense of both phosphite and hypophosphite. At 200°C., however, hypophosphite was transformed into nearly equal quantities of phosphate and phosphite, and at intermediate temperatures the yield of phosphite increased rapidly at first and then decreased slowly as the slow stage of the anneal was reached.

*Table XXXIX.—Chemical Forms of* ${}^{32}P$ *in Potassium Chloride Crystals Irradiated by High Energy Protons*[67]

| Experiment No. | Percentage of ${}^{32}P$ found as | | | |
|---|---|---|---|---|
| | Phosphate | Phosphite | Hypophosphite | Phosphine |
| 1 | 14 | 15 | 51 | 20 |
| 2 | 12 | 11 | 49 | 28 |
| 3 | 15 | 17 | 50 | 18 |
| 4 | 13 | 12 | 41 | 35 |
| 5 | 11 | 10 | 41 | 38 |
| 6 | 12 | 9 | 27 | 52 |

The explanation of these phenomena proposed by the authors is based on the formation of Frenkel defects by interaction of the high energy protons with the ions of the lattice and the production of high temperatures in very small regions near the ends of the tracks of the recoiling phosphorus atoms. These high-temperature effects, which promote some annealing of the lattice, are of very short duration, and, taking into account the ionization potentials of all the species involved, the authors considered that the most probable final oxidation states of the phosphorus atoms are the lower ones (−1, 0 and +1). The rapid stage of thermal annealing, during which a considerable degree of order is restored to the lattice, may then be attributed to electronic transfers between atoms and ions, the phosphorus atoms attaining higher valency states and entering cation sites of the lattice. Since a high positive charge must be balanced by neighbouring cation vacancies it is considered that the slow stage of annealing might result from the diffusion of these vacancies, scattered throughout the lattice, to the neighbourhood of the phosphorus ions. The authors point out that the chemical forms observed would be formed by secondary reactions taking place in solution and the parallel increases of the yields of phosphate and phosphite on annealing at 200°C. might possibly result from the hydrolysis of a species such as $PCl_4$. They therefore postulate two possible schemes for the annealing process:



## Irradiation of Carbon Tetrachloride

The chemical form of radiophosphorus produced by neutron irradiation of carbon tetrachloride has been studied.[50, 61, 63] Govaerts[50] found that on simultaneous irradiation and electrolysis of carbon tetrachloride radiophosphorus was deposited on copper electrodes, but deposition was incomplete. Nesmeyanov[63] showed that the yields of radiophosphorus in the form of phenylphosphonic acid from irradiated mixtures of carbon tetrachloride and benzene or chlorobenzene were the same as those from mixtures of carbon disulphide with the aromatic compounds in the same

*Table XL.—Chemical Forms of* $^{32}P$ *Extracted from Irradiated Carbon Tetrachloride by Various Reagents*[61]

| Series of experiments | Extracting reagent | Percentage of $^{32}P$ | | |
|---|---|---|---|---|
| | | In +5 state | In +3 state | Not extractable |
| I | $H_2O$ | 65 | 10 | 25 |
| | 1·0 N. NaOH | 79 | 19 | 2 |
| | 1·0 N. NaOH* | 97 | 0 | 3 |
| | 1·0 N. $HNO_3$ | 81 | 16 | 3 |
| | 1·0 N. $NHO_3$* | 100 | 0 | 0 |
| II | $H_2O$ | 46 | 25 | 29 |
| | 1·0 N. $H_2O_2$ | 64 | 36 | 0 |
| | 1·0 N. $Na_2SO_3$ | 48 | 52 | 0 |
| | 1·0 N. $Na_2S_2O_3$ | 43 | 56 | 1 |

* Saturated with bromine.

molar proportions. Korshunov[61] investigated the effect of various added compounds on the behaviour of irradiated carbon tetrachloride, and showed that the amount of radiophosphorus which could be extracted from the carbon tetrachloride depended on the reagent used. The amount extracted after the carbon tetrachloride had been refluxed for two hours with an extracting reagent is given in Table XL for various reagents. The distribution of the extractable phosphorus between phosphate and phosphite (the only carriers used) is also given. A small proportion of the radiophosphorus was found to be adsorbed by the containing vessel during the irradiation, and this was increased from a few per cent to 50–80% in the presence of a trace of water, but decreased to zero when an appreciable quantity of water was added before irradiation. The volume of the target material was found to affect the valency state of the radiophosphorus produced, the amount of pentavalent phosphorus increasing with decrease of the target volume. The effect of various added compounds is shown in Table XLI, and the effect of varying the irradiation period in Table XLII. The presence of oxygen dissolved in the target was not found to have an appreciable effect, but high yields of pentavalent phosphorus were observed in the presence of bromine and chlorine, and a marked increase in the amount of pentavalent phosphorus could be brought about by $\gamma$-irradiation. Similar results were obtained for the irradiation of chloroform.

### Diffusion of $^{32}P$ in Crystals

A study of the diffusion of $^{32}P$ in sodium chloride crystals was begun with the object of determining the charge on the phosphorus atoms by comparison of thermal diffusion coefficients with the mobilities in an electric field.[68] This object does not appear to have been achieved, but various aspects of the problem have been investigated. Thin, flat crystals of sodium chloride were irradiated and then heated for periods of up to several hours. The edges of the crystal were trimmed off to eliminate edge effects, and the crystals were then divided into a large number of thin layers

*Table XLI.—Effect of Added Compounds on the Valency State of* $^{32}P$ *in Irradiated Carbon Tetrachloride*[61]

| Compound added | Concentration (ml. per litre of $CCl_4$) | Percentage of $^{32}P$ in pentavalent state |
|---|---|---|
| None | — | 98 |
| $H_2O$ | 0·22 | 86 |
| $H_2O$ | 0·45 | 78 |
| $H_2O$ | 0·7 | 69 |
| $H_2O$ | 0·8 | 68 |
| $H_2O$ | 0·9 | 66 |
| $H_2O$ | 1·6 | 38 |
| 25% $NH_4OH$ | 0·8 | 27 |
| Acetone | 10 | 86 |
| $NH_3$ | saturated | 14 |
| $H_2O$ satd. with $Br_2$ | 0·6 | 98 |

*Table XLII.—Effect of Time of Irradiation on the Valency State of* $^{32}P$ *in Irradiated Carbon Tetrachloride*[61]

| Irradiation period (hrs.) | 12 | 24 | 48 | 84 | 96 | 144 |
|---|---|---|---|---|---|---|
| Yield of $^{32}P$ in +5 state(a) | 84 | 89 | 92 | — | 94 | 98 |
| Yield of $^{32}P$ in +5 state(b) | 47 | 50 | 59 | 79 | — | 86 |

(a) Dry $CCl_4$.
(b) $CCl_4$ containing 0·22 ml. of water per litre.

parallel to the original faces. The concentration profiles of $^{32}$P, shown in Fig. 4, were determined by $\beta$-counting the individual layers, which were obtained in the form of powder. The high concentrations observed at the surfaces were thought to result from an irreversible process of escape, the free energy of the crystal being lowest when all the phosphorus had accumulated on the surface. This surface layer could easily be removed by scraping, and the concentration profile in the remainder of the crystal was found to satisfy a diffusion equation when the period of heating was short enough for the concentration in the middle of the crystal to remain unchanged.[69] Values of the diffusion coefficient obtained in this way are given in Table XLIII, and the activation energy ($W$) was found to be 3·30 ev. per atom. The author concluded that diffusion occurs by way of vacant lattice sites, and taking a value of 2·20 ev. for $\varepsilon_0'$, the energy necessary for the formation of a pair of vacancies,[70] calculated the activation energy for the movement of a phosphorus ion ($\varepsilon_0''$) to be 2·2 ev. from the expression $W=\frac{1}{2}\varepsilon_0'+\varepsilon_0''$.

*Table XLIII.—Diffusion Coefficients for* $^{32}$P *in Sodium Chloride Crystals*[69]

| Temperature (°C.) | 610 | 635 | 690 | 727 |
|---|---|---|---|---|
| Diff. coefficient (cm$^2$. sec$^{-1}$) | $3{\cdot}8\times10^{-10}$ | $1{\cdot}16\times10^{-9}$ | $1{\cdot}27\times10^{-8}$ | $5{\cdot}73\times10^{-8}$ |

The accumulation of radiophosphorus on the surface of the crystal suggested the possibility of separation of $^{32}$P and of $^{35}$S (which diffused in a similar way) from the sodium chloride. It was found that the radiosulphur could be removed by passing a stream of hydrogen over the heated crystal. The radiophosphorus was carried to the cooler parts of the apparatus by the very small amounts of sodium chloride which evaporated from the crystal surface,[71] and could be recovered by treating the deposit

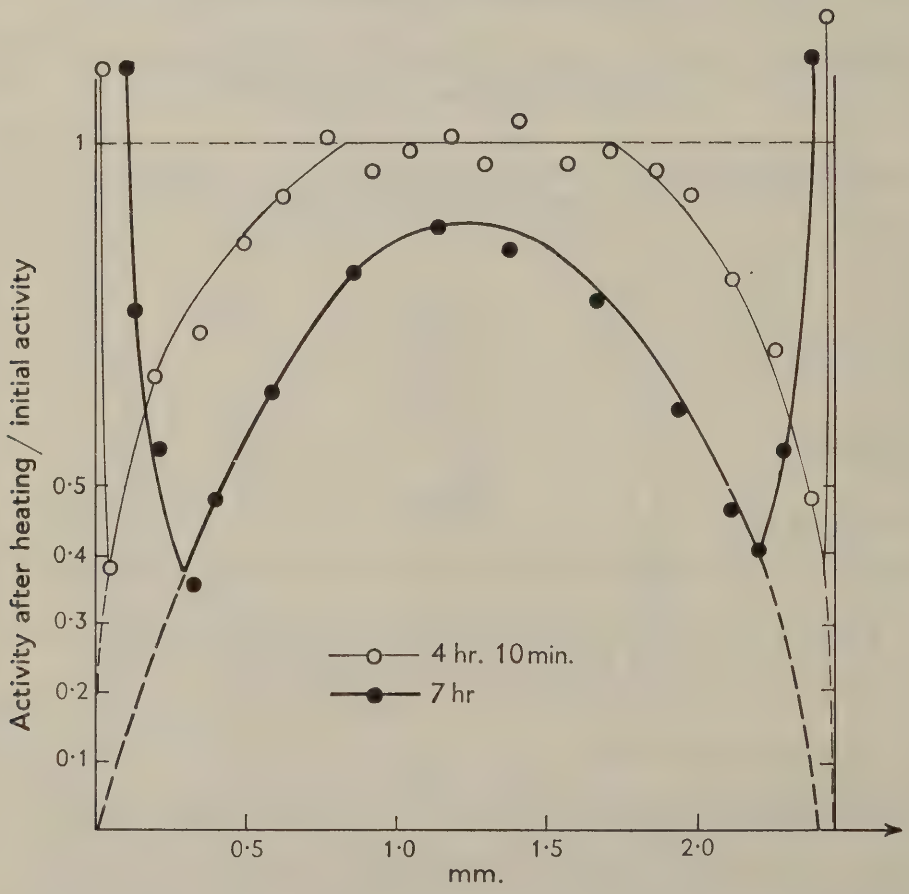


FIG. 4.—Diffusion of $^{32}$P at 660°C. in a sodium chloride crystal for various times

so formed with water. More than half of the radiophosphorus was separated in this way in one experiment. Yields of 85% were obtained by the use of finely powdered sodium chloride; after removal of the radiosulphur, the radiophosphorus was carried by a stream of chlorine into a receiver containing a small quantity of water.[72] Oxygen had to be rigidly excluded from the system, as the presence of trace amounts prevented the escape of phosphorus, presumably by converting it to oxyanions. The whole of this work is summarized and discussed by the author in a later paper.[73]

The problem of determining the charge on the phosphorus atoms has recently been taken up again,[74] the radiophosphorus in this case being produced by the spallation of potassium chloride crystals by 660 Mev. protons. The nuclear reactions involved have already been mentioned in connection with a study of the chemical state of radiophosphorus in potassium chloride crystals.[67] The concentration profiles and diffusion coefficients obtained were similar to those observed by Chemla for neutron-irradiated sodium chloride,[68-9] and the activation energy obtained (3·2 ev. per atom) is very close to that for diffusion in sodium chloride. Measurements of the mobility in an electric field combined with the diffusion data led to a value of 0·191 ± 0·045 electron charge units for the charge on the phosphorus atom, and this small negative effective charge was interpreted as being the result of a strong interaction between phosphorus ions and the anions of the lattice which would cause phosphorus ions to be dragged towards the anode. The authors consider that phosphorus ions occupy potassium sites of the lattice and exist as complexes of the form $[P^{5+}.4K_{\square}^{+}.6Cl^{-}]$, where $K_{\square}^{+}$ represents a vacant potassium ion site (this view is based partly on the results of the annealing experiments already described,[67] which indicated that in annealed crystals a large proportion of the phosphorus is in the +5 state). The presence of large amounts of radiophosphorus on the crystal surfaces was thought to be due to occupation of surface lattice sites by phosphorus ions or to formation of oxides.

## CHEMICAL STATE OF $^{32}$P PRODUCED BY SPALLATION REACTIONS

The chemical state of $^{32}$P produced by spallation of potassium chloride has already been mentioned.[67] Many other spallation reactions led to its production but the chemical form of the radiophosphorus has not usually been investigated. The reaction of $^{14}N^{6+}$ ions with $^{27}$Al has been studied,[75] however, and has given results very different from those obtained by other nuclear processes. When a bombarded aluminium foil was dissolved in sodium hydroxide solution in the absence of air no phosphate could be observed, a third of the radiophosphorus was found in the form of reduced oxyanions, and the remainder as phosphine. The authors tentatively suggested that the radiophosphorus must exist in the target in very low oxidation states or as elemental phosphorus, which would react with water, hydroxyl ions, or the hydrogen produced on dissolution of the aluminium. The yields of the various products would then result from competition between reactions of the type:

$$P + 3H \rightarrow PH_3 \quad \text{and} \quad P + 2H_2O \rightarrow H_3PO_2 + H$$

or

$$P^+ + 4H \rightarrow PH_3 + H^+ \quad \text{and} \quad P^+ + 2H_2O \rightarrow H_3PO_2 + H^+$$

## EXCITED-ATOM CHEMISTRY OF $^{33}$P PRODUCED BY THE $^{33}$S($n$, p)$^{33}$P REACTION

Very little attention has been given to this problem, but Nilsson[56] was unable to find any significant difference between the chemical forms of $^{32}$P and $^{33}$P in irradiated sulphur (Table XXII). Recently some work on this subject has been carried out by Lindner,[62] who irradiated anhydrous sodium sulphite in the thermal columns of JEEP and BEPO. The results obtained from the target irradiated in BEPO (Table XLIV) do not indicate any difference in behaviour between the two isotopes, but a greater proportion of the $^{33}$P than of the $^{32}$P was found in the orthophosphate fraction obtained from targets irradiated in JEEP. The results of the experiments in JEEP are, however, rather uncertain, and subsequent work on the neutron bombardment of a number of sulphates and sulphites at dry ice temperature has failed to reveal any significant difference between the behaviour of $^{32}$P and $^{33}$P.[76]

*Table XLIV.—Comparison of Chemical Forms of* $^{32}$P *and* $^{33}$P *in Irradiated Anhydrous Sodium Sulphite*

| Reactor | Percentage of radiophosphorus in valency states other than +5 | |
|---|---|---|
| | $^{32}$P | $^{33}$P |
| JEEP | 38–44 | 19–25 |
| BEPO | 16·7 | 16·7 |

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### SECTION XXXVII

# APPLICATIONS OF RADIOPHOSPHORUS

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OF the radioactive isotopes of phosphorus only two have long enough half-lives to be of general use, viz., $^{32}P$ with a half-life of about 14 days and $^{33}P$ with a half-life of about 25 days. Although it would appear that $^{33}P$ should be as useful as $^{32}P$, and in certain applications would have advantages in view of its longer half-life and lower $\beta$ energy, the absence of any commercial process for its production has hitherto prevented its use. It has been suggested that the two isotopes could be used for the double labelling of phosphorus compounds,[1] and it has been shown that the relative amounts found in rainwater as a result of cosmic ray bombardment of atmospheric argon can serve as an indicator of the movement of large air masses.[2]

In contrast to $^{33}P$, $^{32}P$ is one of the most widely used radioisotopes, although its chemical applications are very limited, its principal uses being in medicine, biology and biochemistry. A brief outline of its uses will be given here, and the general references given below should be consulted for more detailed information.

## Applications in Medicine, Biology and Biochemistry

The absence of $\gamma$-radiation makes $^{32}P$ particularly suitable for local diagnostic purposes; it is preferentially taken up by malignant tumours, and can therefore be used in the diagnosis of tumours of the eye[3] and breast,[4] and for the accurate location of brain tumours during surgery.[5] The determination of blood volume can readily be carried out by an isotopic dilution technique.[6] $^{32}P$ is used as a therapeutic agent in the treatment of leukaemia and polycythemia vera,[7] and has also been used in the treatment of latent, resistant syphilis.[8] More detailed information can be found in a number of reviews,[9] some of which include extensive bibliographies.

Some of the earliest references to the use of radiophosphorus are in the field of biological research: Hevesy used $^{32}P$ in a study of phosphorus metabolism in rats,[10] and showed that the phosphorus in the leaves of plants is in a mobile state and that interchange between different leaves takes place.[11] Biological applications were developed very rapidly and reviews were published as early as 1938 and 1939.[12] Radiophosphorus has since been widely used in studies of metabolism and in the determination of the structures of complex compounds such as enzymes. The behaviour of insects such as bees and ants has been studied by marking insects by means of radioactive food and then following their distribution among the other members of the community.[13] These biological and biochemical applications have been fully described in a number of books and papers.[14]

## Applications in Agriculture

By the use of $^{32}P$-labelled phosphorus compounds it has been possible to study the behaviour of phosphates in soil and the uptake of phosphates by plants. In particular this technique enables exchange reactions in the soil to be studied.[15] Radiophosphorus has also been used in the evaluation of fertilizers,[16] and in studies of soil erosion.[17] The agricultural applications of radiophosphorus have been described,[18] and a number of papers on this subject are available.[19]

## Industrial Applications

The effect of radiophosphorus on the rate of digestion of sewage has been studied. Several workers have observed no significant effects with carrier-free $^{32}P$ at concentrations of up to 400 mc./l.[20] Grune[21] found that there was a reduction in the rate of gas production with 50 mc./l. incorporated into $KH_2PO_4$, but since inactive $KH_2PO_4$ was found to have a similar effect this behaviour was attributed to chemical toxicity. Radiophosphorus has been used as an indicator in following the course and dilution of sewage,[22] and has also been used to study the possibility of producing potable water by the decontamination of radioactively contaminated surface water.[23]

By the use of radiophosphorus as an indicator the course of many industrial processes can be followed in detail. The movement of the charge in a blast-furnace has been followed by introducing $^{32}P$ into the coke and limestone[24]; it has been observed that the rate of movement is greatest at the top centre of the furnace and that the lime precedes the coke. Introduction of $^{32}P$ through the tuyeres followed by monitoring of the iron showed that there was no significant circulation of iron in the hearth. Other problems in the iron and steel industry which have been tackled with the aid of radiophosphorus include investigations of the process of crystallization in ingots and castings[25] and of the characteristics of a mixer for basic Bessemer pig iron,[26] and the determination of the amount of slag in a basic open-hearth furnace during the period of pure boiling.[27]

Autoradiography with $^{32}P$ has been used to establish the distribution of phosphorus in welds,[28] and to measure the abrasion of rubber on a steel plate.[29] In this case the $^{32}P$ was incorporated in the rubber, and the steel was autoradiographed after the experiment. The degree of mass transfer between steel specimens has been determined by the incorporation of $^{32}P$ in one of the specimens.[30] The behaviour of lubricating oils containing labelled additives has been followed, and information obtained on the stability of the solutions[31] and on the thickness of extreme pressure films.[32]

Other technological applications of radiophosphorus include studies of the flow-time distribution of water in heat exchangers,[33] grain boundary segregation in iron–phosphorus alloys,[34] and the migration of elements in the processing of $Al_2O_3$.[35] The behaviour of protective phosphate coatings on iron, steel, and zinc,[36] and the corrosion of aluminium by alkaline phosphates[37] have been studied, and a method for the detection of dye contamination in the multicolour printing of textiles has been devised.[38] A measure of the deterioration of rubber resulting from the action of organic liquids can be obtained from the uptake of labelled radiophosphorus,[39] and measurement of the back-scattering from glass of $\beta$-particles from radiophosphorus has enabled the amount of lead in the glass to be determined without affecting the glass in any way.[40]

$^{32}P$ can be used in the production of self-luminous materials by mixing it with a zinc sulphide type phosphor and polystyrene,[41] the amount of getter material applied to glow lamps can be checked by mixing $^{32}P$ with the getter,[42] and autoradiographic techniques with $^{32}P$ have even been used to study pearl formation in oysters.[43]

## Applications in Physics

The fact that in the irradiation of sulphur $^{32}P$ is formed only as a result of fast neutron bombardment means that the amount of $^{32}P$ formed can be used as a measure of the fast neutron flux or dose,[44] and this is the principal physical application of $^{32}P$. Since there is a minimum 'threshold' neutron energy, this reaction can be used along with others to obtain information about the neutron energy distribution. The ready availability of $^{32}P$ and the absence of $\gamma$-rays make it an obvious choice when a $\beta$ source is required. It has been used for instance to study the sensitivity of photographic film and plates[45] and in the development of a scintillation counter for $\beta$-radiation dosimetry.[46] The dependence of the Hall mobility of germanium semiconductors on the concentration of phosphorus has been studied with the aid of radiophosphorus.[47]

## Applications in Chemistry

Apart from studies of excited atom chemistry, which are discussed in another section, the chemical applications of radiophosphorus fall into two main groups:—those applications in which the presence of a radioactive atom is of fundamental importance, such as studies of self-diffusion and exchange reactions, and those in which the radioactive atom is used as a tracer so that the amount of phosphorus in a sample or in a particular chemical form can be determined without the need for complete chemical analysis. Occasionally $^{32}P$ is used as a source of $\beta$-radiation, since accurately standardized sources can easily be obtained. For example, it has been used in solution as an internal source for the determination of the radiolytic yield of $Fe^{3+}$ from ferrous ammonium sulphate solution.[48]

The behaviour of a substance in trace quantities is often different from that observed in larger quantities, since it often happens that solubility products are not exceeded, and the tracer may be entrained by precipitates or adsorbed on the walls of vessels. The errors resulting from adsorption on glassware have been studied and it has been shown that these errors can be reduced by pretreatment of the glassware with silicones.[49] Experiments carried out by Yuan[50] indicated that differential adsorption of $^{31}P$ and $^{32}P$ could occur, leading to loss of $^{32}P$ by adsorption on glassware or on soil even in the presence of carriers. This kind of effect is particularly likely to occur if some of the $^{32}P$ is not in the same chemical form as the carrier, and Olsen and Watanabe,[51] using pure materials, were unable to detect any differences between the two isotopes. The effects of temperature, acid concentration, and cupric ion concentration on the entrainment of $^{32}P$ on cupric sulphide precipitates have been studied by Kar and Rangan,[52] and a general description of the behaviour of trace quantities of radioisotopes including $^{32}P$ has been given by Lavrukhina.[53]

## Studies of Isotopic Exchange

Some of the isotopic exchange reactions which have been studied are given in Table I. In most cases no exchange could be detected beyond the limits of experimental error, and where exchange did occur it was not generally attributable to a simple exchange of phosphorus atoms. Thus the exchange between phosphorus tri- and penta-chlorides was attributed[56] to a slowly attained equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, and the exchange between disodium orthophosphate and tricalcium orthophosphate was due to exchange of the phosphate anion.[67]

The absence in general of exchange of phosphorus atoms between different compounds of phosphorus is of considerable importance, since it enables $^{32}P$ to be used as a tracer with reasonable confidence.

## Studies of Diffusion by means of $^{32}P$

The diffusion and migration of phosphorus compounds can readily be followed in solution by following the change in activity as a function of time, and in solids by studying the activity profile in the substrate. The self-diffusion of phosphorus in solutions of $NaH_2PO_4$ has been investigated, and the activation energy and dependence on concentration determined.[71] It was found that for concentrations above 0·005 M. the diffusing species was almost entirely the ion $H_2PO_4^-$, but that at much lower concentrations the ion $HPO_4^{2-}$ began to play a significant part. Migration of $H_3PO_4$ through a collodion membrane has been found to be hindered at low concentrations.[72] This hindrance was increased by oxidation of the membrane, but decreased by an increase in ionic strength. The diffusion coefficients of phosphates in gelatin have been found to be dependent on the concentration gradient,[73] and lower values have been obtained in self-diffusion experiments where there is no concentration gradient.[74] Self-diffusion of $H_3PO_4$ in charcoal has also been studied.[75]

The migration of $^{32}P$ in apatite has been found to take place both on the surface and through the bulk of the crystals and does not appear to be a diffusion process.[76]

*Table I.—Isotopic Exchange Reactions of Phosphorus*

| Reactants | Experimental conditions | Remarks | Ref. |
|---|---|---|---|
| $P_4$, $PCl_3$ | $CS_2$ soln. | 4% exchange in a few minutes, 30% exchange in a few days. | 54 |
| Red P, $PCl_3$ | 3 hr. at room temp. | <2% exchange | 55 |
| | 73 hr. at 30°C. plus 62,100 *R X*-rays | <2% exchange | |
| $PCl_3$, $PCl_5$ | $CCl_4$ soln., 0·1°C. | 1st order rate constants $9{\cdot}4\times10^{-4}$ hr.$^{-1}$ | 56 |
| | 25°C. | $1{\cdot}01\times10^{-2}$ hr.$^{-1}$ | |
| | 50°C. | $7{\cdot}9\times10^{-2}$ hr.$^{-1}$ | |
| $PCl_3$, $PSCl_3$ | 2 hr., 163°C. | <2% exchange. | 55 |
| $PCl_3$, $POCl_3$ | 23 days, 250°C., white light. | No detectable exchange. | 57 |
| | Subjected to u.v. light. | Exchange observed; enhanced by hydrolysis products. | |
| | Subjected to $\gamma$-rays. | Exchange rate proportional to dose. | |
| $POCl_3$, $H_3PO_4$ | Up to 150°C. | Half-time of exchange 3 hr. | 58 |
| $PSCl_3$, $H_3PO_4$ | ,, ,, ,, | ,, ,, ,, ,, 36 hr. | 58 |
| $H_3PO_2$, $H_3PO_3$ | Aq. soln., room temp. and 70°C. Also in presence of $I_2$ or $I^-$. | No detectable exchange after several hours. | 59 |
| $KH_2PO_2$, $KH_2PO_3$ | Aq. soln., room temp. and 70°C. Also in presence of $I_2$ or $I^-$. | No detectable exchange after several hours. | 59 |
| $NaH_2PO_2$, $NaH_2PO_4$ | Aq. soln., 80 hr., up to 280°C. | No detectable exchange. | 60 |
| $NaH_2PO_2$, $NaNH_4HPO_4$ | Aq. soln., 10 days at room temp. followed by 1 day at 100°C. | ,, ,, ,, | 61 |
| $NaH_2PO_2$, sodium glycerophosphate | Ditto. | ,, ,, ,, | 61 |
| $(C_2H_5O)_3P$, $C_2H_5PO(OC_2H_5)_2$ | 160 hr. at room temperature, 6 hr. at 100°C. | ,, ,, ,, | 62 |
| $H_3PO_3$, $H_3PO_4$ | Acid and alkaline solns., 20°–100°C., up to 26 days. | ,, ,, ,, | 63 |
| $H_3PO_3$, $H_3PO_4$ | Aq. soln., 80 hr., up to 280°C. | ,, ,, ,, | 60 |
| $Na_2H_2P_2O_6$, $Na_4P_2O_7$ | pH 1–10, 25°–90°C. | ,, ,, ,, | 64 |
| $Na_2H_2P_2O_6$, $NaH_2PO_4$ | ,, ,, ,, | ,, ,, ,, | 64 |
| '$HPO_3$', $H_4P_2O_7$ | pH 2·3, 27°–100°C., 0·5–1·5 min. | ,, ,, ,, | 65 |
| '$HPO_3$', $H_3PO_4$ | pH 2–12·5, 21°–100°C., 2–20 min. | ,, ,, ,, | 65 |
| '$(NaPO_3)_6$', $(NaPO_3)_3$ | pH 2–10, 0°–100°C., 0·17—90 hr. | ,, ,, ,, | 66 |
| '$(NaPO_3)_6$', $NaH_2PO_4$ | 25°C., 25 hr. | ,, ,, ,, | 66 |
| $H_4P_2O_7$, $H_3PO_4$ | pH 2–12·2, 25°–100°C., 1–100 min. | ,, ,, ,, | 65 |
| $Na_2HPO_4$, $Ca_3(PO_4)_2$ | 3 days, 18°C. | 3·1% exchange of $PO_4^{3-}$ | 67 |
| | 180°C. | 8·1% exchange of $PO_4^{3-}$ | |
| $Na_2HPO_4$, $(C_2H_5O)_3PO$ | Dioxan soln., 100°–300°C., 20–30 hr. | No detectable exchange. | 68 |
| $Na_2HPO_4$, $(n\text{-}C_4H_9O)_3PO$ | Dioxan soln., 100°–300°C., 20–30 hr. | ,, ,, ,, | 68 |
| $H_3PO_4$, $(n\text{-}C_4H_9O)_3PO$ | Aq. and org. phases shaken together, acid and alk, solns., 1 min.–1 month. | ,, ,, ,, | 69 |
| $Na_2HPO_4$, $(iso\text{-}C_4H_9O)_3PO$ | Dioxan soln., 100°–300°C., 20–30 hr. | ,, ,, ,, | 68 |
| $Na_2HPO_4$, $(C_6H_{13}O)_3PO$ | Dioxan soln., 100°–300°C., 20–30 hr. | ,, ,, ,, | 68 |
| $H_3PO_4$, $(CH_3C_6H_4O)_3PO$ | Dioxan soln., 100°–300°C., 20–30 hr. | ,, ,, ,, | 68 |
| $Na_3PO_4$, glucose-1-phosphate | pH 8, 37°C., 3 hr. | ,, ,, ,, | 70 |
| $Na_3PO_4$, 2,3-diphosphoglyceric acid | ,, ,, ,, | ,, ,, ,, | 70 |
| $Na_3PO_4$, adenylic acid | ,, ,, ,, | ,, ,, ,, | 70 |
| $Na_3PO_4$, adenosine triphosphate | ,, ,, ,, | ,, ,, ,, | 70 |

Diffusion coefficients have been determined for the migration of phosphate from tricalcium phosphate into calcium oxide[77] and for tritolyl phosphate in polystyrene.[78]

The diffusion of $^{32}P$ in single crystals of sodium chloride has been studied by Chemla[79] and has been more fully discussed in the section on excited atom chemistry (p. 1357). Other problems studied by diffusion methods include the chromatographic separation of iron and zinc by precipitation when their chlorides diffuse into gels containing $K_2HPO_4$,[80] the formation of complex phosphotungstate ions in solution,[81] and the behaviour of phosphates in soils.[82]

## Applications to Analytical Chemistry

Table II lists some of the analytical uses of radiophosphorus. $^{32}P$ is sometimes used in the development of analytical procedures since the relative activities of various samples obtained by the chemical procedure can indicate the distribution of the phosphorus compound under investigation. It has been used in this way in studies of chromatographic methods of analysis of mixtures of phosphorus compounds,[98] in the study of phosphate separations in semi-micro qualitative analysis,[99] in investigations of volumetric methods of determination of phosphorus in ferroniobium[100] and ferrotitanium,[101] and in the development of analytical methods for the determination of small quantities of elements in complex mixtures.[102] The composition of phosphotungstates has been determined by double labelling with radioactive phosphorus and tungsten; the difference between the half-lives enabled the amounts of phosphorus and tungsten to be determined.[103]

*Table II.—Analytical Applications of Radiophosphorus*

| Substance determined | Other substances present | Remarks | Ref. |
|---|---|---|---|
| P | Al alloys or $Al_2O_3$ | Activation analysis. | 83 |
| P | Ge | ,, ,, | 84 |
| P | $I_2$ | ,, ,, | 85 |
| P | Si | ,, ,, | 86 |
| P | Se or Te | ,, ,, | 87 |
| $Na_2HPO_4$ (0·001 M.) | $NH_3$ and $NH_4Cl$ soln. | $PO_4^{3-}$ pptd. with $MgCl_2$. $^{32}P$ used as end-point indicator. | 88 |
| $K_3PO_4$ | $KNO_3$ | Determination of trace impurity in study of zone-melting. | 89 |
| $Na_5P_3O_{10}$<br>$Na_4P_2O_7$ | Other phosphate anions, sulphate, silicate, anionic detergents. | Isotopic dilution. $Na_5P_3O_{10}$ and $Na_4P_2O_7$ pptd. by addition of alcohol to aqueous solution. | 90 |
| Calcium hydroxyapatite | Polystyrene | Higher concn. found in larger beads. | 91 |
| Al, In, La, Ce, Zr. | Other metals. | Determined as phosphates with $Na_2H^{32}PO_4$ or $(NH_4)_2H^{32}PO_4$ after partial chemical separation. | 92 |
| Mg | | Pptd. with $Na_2H^{32}PO_4$. Activity of ppt. determined. | 93 |
| Mg | $NH_3$ and $NH_4Cl$ | Pptd. with $Na_2H^{32}PO_4$. End-point determined by change in activity of solution, or activity of ppt. measured. | 94 |
| Mg and Ca | Portland cement. | Ca and Mg separated in preliminary step. Pptd. with $(NH_4)_2H^{32}PO_4$ soln. Activity of soln. measured before and after pptn. | 95 |
| $MgCl_2$ (0·01 M.) | $NH_3$ and $NH_4Cl$ soln. | Mg pptd. with $Na_2H^{32}PO_4$. Presence of $^{32}P$ in soln. used as end-point indicator. | 88 |
| Uranyl acetate (0·005 M.) | $NH_4$ acetate | U pptd. with $Na_2H^{32}PO_4$. End-point corresponds with minimum activity in soln. | 88 |
| Mn and Zn | | Pptd. with $(NH_4)_2H^{32}PO_4$ soln. Activity of soln. measured before and after pptn. | 96 |
| F | Na, K, Mg, Ca. | Chromatographic technique with $ZrOCl_2$ and $H_3{}^{32}PO_4$. | 97 |

**Refs. p. 1367**

## Other Chemical Applications of $^{32}$P

Radiophosphorus has been used as an indicator in studies of the solubility of mono-, di-, and tri-butyl phosphates[104–5] and of thorium phosphates,[106] in adsorption studies,[107–8] in surface area determination,[109] and in studies of losses of non-volatile substances during freeze-drying.[110] The chemistry of the mono-, di-, and tri-butyl phosphates has been extensively studied with the aid of radiophosphorus. The aspects studied include the hydrolysis[111] of tributyl phosphate, the preparation[112] and separation[113] of the various butyl phosphates, and the distribution of these compounds in various systems.[104, 114]

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### SECTION XXXVIII

# THE RADIATION CHEMISTRY OF PHOSPHORUS AND ITS COMPOUNDS

### BY T. FFRANCON WILLIAMS

THIS section reviews the literature concerning the chemical changes which result from the irradiation of phosphorus compounds. Photochemical transformations, as well as the effects of ionizing radiation, are included in this survey, but the discussion of nuclear recoil effects accompanying the formation of radioactive phosphorus atoms is limited to the contribution made by these latter studies to an understanding of the chemistry of radiation-induced changes. These terms of reference enable the topic to be discussed in the widest sense and this approach has been dictated by the fact that much of the available information is scattered and fragmentary. Although only a few concerted and comprehensive studies have been reported hitherto, these are selected for more detailed discussion since they afford a few guiding principles to an appreciation of the chemistry which is involved.

At the outset it seems appropriate to mention some of the physical and physicochemical factors which underlie the absorption of radiation within the range of energy spectrum corresponding to the production of chemical changes. When a quantum of visible or ultra-violet light of wave-length greater than 2000 A. is absorbed by a molecule, an electron is promoted to a higher energy level. The subsequent fate of an excited molecule often involves a variety of competing processes which depend, in general, on the physical state of the absorbing species and on the intimate chemical environment. From a chemical standpoint, an excited molecule may undergo homolytic dissociation to give free radicals or it may react in the excited state; in addition, there is the possibility of the activated molecule undergoing energy transfer with another molecule resulting in the sensitization of the latter. Other processes can lead to the degradation of the initial excitation energy, either by internal transfer to vibrational and rotational degrees of freedom or by light emission from excited levels to the ground state as observed in fluorescence and phosphorescence. In some molecules triplet states may be excited directly or by a transition from a higher singlet state following light absorption; the lifetime of a triplet state measured in terms of the duration of light emission from this excited state, where the absorbing molecule is in the gas phase or in an inert chemical environment, can often extend for $10^{-3}$ sec. By comparison, singlet excited states usually have much shorter lifetimes, *ca.* $10^{-8}$ sec. or less, and consequently the triplet state is more prone to take part directly in chemical reaction. In the case of simple molecules, the primary photochemical act can often be specified unambiguously, but for complex polyatomic molecules, the processes of intra- and intermolecular energy transfer referred to above are far from well understood in their entirety. For a detailed discussion of these topics, the reader is referred to several texts and review articles.[1-8,132]

As the energy of a photon is increased beyond several electron volts, the contribution of photo-ionization to the mechanisms of energy loss becomes of primary importance. The term ionizing radiation is now employed to cover high energy quanta extending from the photo-ionization limit to the highest gamma-ray energies encountered and also includes beams of fast charged particles such as electrons, protons and α-rays. In the case of electromagnetic radiation, the photon energy is passed on to the absorbing medium as energetic electrons derived from photoelectric absorption and Compton scattering with a contribution from pair production at quantum energies exceeding 1 Mev.; the relative importance of these processes as a function of the atomic number of the absorbing material and photon energy is well established.[9] Information from the physics of energy loss by charged particles can be used to derive the spatial distribution of ionization events relative to the path of the primary particle[10]; in this connection it is often convenient to use the term linear energy transfer (LET) to describe the energy loss in units of ev. per A. The passage of heavy charged particles results in the emission of adjacent low-energy secondary electrons with the formation of dense columnar regions of ionization, whereas fast electrons only lose energy at widely separated intervals (*ca.* 1000 A.) in condensed media. A consequence of this different geometrical distribution is that the possibility of interaction between the primary products of chemical change is much more likely at a high rate of LET.[10] Thus it is found that for aqueous solutions, the quantitative chemistry is highly dependent on the energy of the incident particle,[11] although it should be noted that this behaviour is not universal and, for the case of organic systems, only aromatic compounds have hitherto been found to display a dependence of chemical yield on ion density.[12] In addition to the ionization of molecules, there is evidence that direct excitation also represents an important mode of energy loss from the charged particles to the medium. Measurements of $W$, the mean energy required to form an ion pair in irradiated gases, give values[13] in considerable excess of the ionization potential and, although part of this difference must be attributed to the excitation of the ion, it is generally assumed that direct excitation and ionization events are comparable in magnitude.

The electronic processes referred to above occur with extreme rapidity (*ca.* $10^{-16}$ sec.); the subsequent behaviour of the positive parent ions, excited molecules and thermalized electrons (or negative ions) determines the overall chemistry of any system. The effect of physical state is clearly of paramount importance since the neutralization time of an ion in a gas at atmospheric pressure is about $10^{-3}$ sec., whereas the corresponding interval in the liquid phase is usually estimated[14] at about $10^{-12}$–$10^{-13}$ sec. Consequently ion-dissociation processes must be extremely fast to compete with neutralization in the liquid state and these are probably limited to exothermic reactions.[15] On the other hand the fragmentation of gaseous ions can be appreciable, even for endothermic dissociation, in a time of $10^{-10}$ sec. which corresponds to the interval between collisions at atmospheric pressure.[16] Apart from undergoing dissociation, parent ions may also react in ion-molecule processes which in some instances have been shown to occur on every collision in the mass spectrometer.[17] The importance of ions in the radiation chemistry of gases was originally emphasized by Lind.[18] Both ion-molecule and ion-dissociation processes can therefore make important contributions to the formation of free radicals and molecular products, particularly for gaseous systems, and there is now a substantial body of experimental evidence to support this contention.[19-20] One particular advantage which accrues from the evaluation of ionic processes is that the reactions of a polyatomic molecule-ion can often be specified with some degree of certainty. In considering the behaviour of excited polyatomic molecules, it is rarely possible to predict the nature of the reactivity unless a well-defined (e.g. triplet) state is concerned. The neutralization of an ion has often been represented unequivocally as leading to the formation of another excited molecule. An alternative process is the elimination of a proton from the prevailing ion in the case where the latter contains hydrogen,[13, 21] leading to hydrogen atom formation:

$$t.\mathrm{C_4H_9}^+ + e^- \rightarrow iso\mathrm{C_4H_8} + \mathrm{H}$$

It is also conceivable that in the presence of substances with high electron affinity, electron capture may occur with negative ion formation before neutralization.[22-4] In summary, we note that the processes following (or attendant upon) ionization, excitation, electron capture and neutralization lead to a wide spectrum of possible intermediate and molecular products. The transient chemical species are undoubtedly radicals and ions, but their nature and relative importance are largely determined by the chemical structure and physical state of the system. This chemical effect of ionizing radiations is expressed in terms of an energy yield or 'G unit', defined as the number of molecules produced or decomposed for each 100 ev. of energy absorbed from the radiations.

The chemical effects of thermal neutron capture are of special interest in the case of phosphorus, but this is a more specialized branch of radiation chemistry since the emphasis is placed mainly on the chemical fate of the radioactive atom. Nevertheless, it is important to consider the effect of energy dissipation during nuclear recoil since both the dense concentration of chemical decomposition products and, possibly, the transient high temperatures generated along the track would be expected to affect the ultimate result; these aspects are referred to below.

Although it is something of a misnomer to write of the radiation *chemistry* of phosphorus, it is appropriate to begin by noting the effects of radiation on the different allotropic and physical states of the element. Phosphorus vapour is known[25] from electron diffraction studies to be made up of $P_4$ molecules as regular tetrahedra, but above 800°C. the $P_4$ thermally dissociates to give $P_2$ molecules. Robinson[26] determined the ionization potential of neutral phosphorus to be less than 10·9 ev. by an optical spectroscopic investigation of the discharge emitted by a Geissler tube containing phosphorus vapour. It was noted in this work that the yellow phosphorus vapour quickly polymerized in the discharge tube to give a more stable brownish yellow substance of low vapour pressure. By the same technique, the second ionization potential of phosphorus was calculated to be 19·56 ev. In a second investigation of phosphorus spectra, using a hot spark discharge between beryllium electrodes containing red phosphorus, it was further established[27] that the ionization potentials corresponding to the formation of $P^{3+}$, $P^{4+}$ and $P^{5+}$ are 30·012 ev., 51·016 ev. and 64·698 ev., respectively. A more recent determination[28] of the first and second ionization potentials gives respective values of 10·48 ev. and 19·72 ev. which are in good accord with the previous data. Kerwin[29] has studied the mass spectrum of phosphorus; the element was evaporated from a hot filament and bombarded with electrons. No appearance potential measurements at low voltages were carried out. With 70 volt electrons, the mass spectrum showed the following relative ion yields: $P_1$ 16; $P_2$ 50; $P_3$ 6; $P_4$ 100; $P_5$, $P_6$ and $P_7$ none; $P_8$ 0·5; and the element was found to be largely monoisotopic. The observation of $P_8$ units in this work is interpreted as supporting the theory put forward by Pauling and Simonetta[30] for the mechanism of formation of red phosphorus from white phosphorus. According to this view one of the bonds of tetrahedral white phosphorus breaks open and the open tetrahedra then join in long chains forming amorphous red phosphorus; such chains are thought, however, to be unstable and to break down readily to give molecules made up of multiples of $P_4$ so that a low percentage of $P_8$ molecules would be expected in red phosphorus. The presence of appreciable amounts of $P_2^+$ ions in the mass spectrum suggests that the dissociation of the parent ion, $P_4^+$, occurs readily:

$$P_4^+ \rightarrow P_2^+ + P_2$$

There are several reports[31] which indicate that ultra-violet radiation catalyses the thermal conversion of white phosphorus to red phosphorus; the latter process[32] is ordinarily a first order reaction in the temperature range 250°–350°C. with an activation energy of 38 kg.-cal./mole. Rathenau[33] has studied the photochemical precipitation of red phosphorus from a solution of white phosphorus in carbon disulphide; the reaction velocity is again first order in concentration of white phosphorus and it has been suggested that the mechanism involves the dissociation of $P_4$:

$$P_4 \rightarrow 2P_2$$

the $P_2$ molecules recombining to form red phosphorus. Some observations[34] on the effect of pile irradiation on white phosphorus also indicate that conversion to red phosphorus occurs.

A modification of the chemical properties of red phosphorus after irradiation with neutrons in a reactor has been described[35] in which it was found that an irradiated sample was more easily oxidized by atmospheric oxygen than the inactive material. Thus about 1·0–1·5% of the total mass of an irradiated sample dissolved in an aerated aqueous solution to yield several oxy-acids of phosphorus. However, if the dissolution was attempted in the absence of air, only a small mass of the active phosphorus was found in solution. Evidence that the radioactive atoms dissolved more readily, in the presence of oxygen, than inactive material is suggested by the higher specific activity of the aqueous extract relative to insoluble phosphorus. The irradiation of orthorhombic black phosphorus[36] in a reactor for one month resulted in 0·03% expansion of the *c* axis as evidenced[37] by measurements on the broadening of the (00*l*) *X*-ray diffraction peaks. It is interesting that the same irradiation dose did not affect the lattice parameters of close-packed metallic crystals. The authors suggest[37] that the expansion is the result of the displacement of phosphorus atoms from the layers into interstitial lattice positions, and that (since the *c* direction is thought to be highly elastic under strain) even small disturbances between the planes would be sufficient to cause the observed effect. It was also noted that the *X*-ray diffraction pattern of the irradiated black phosphorus revealed a number of new lines which could partly be assigned to one of the several known forms of red phosphorus.[38] Although this finding suggests that black phosphorus can revert to the less stable red phosphorus under neutron bombardment, this conclusion must still be regarded as tentative since some characteristic lines of red phosphorus were not observed.

At this point it seems pertinent to mention that phosphorus atoms born in nuclear reactions do not appear in the form of elementary phosphorus. This conclusion rests on the study by Carlson and Koski[39] of the phosphorus products arising from the nuclear reaction $^{35}$Cl $(n, \alpha)^{32}$P in neutron-irradiated potassium chloride crystals. The effect of pre-irradiation treatment, particularly the out-gassing of the sample, affected the distribution of $^{32}$P in the various 'oxidation states' as determined by the use of phosphine, hypophosphite, phosphite and phosphate as carriers. The use of the term 'oxidation state' to denote the nature of phosphorus combination with other elements has been criticized by Van Wazer.[40] In any case, it appears to be a doubtful assumption that the valence state of phosphorus in the potassium chloride crystal necessarily corresponds to the final 'oxidation state' of the element after dissolution and, presumably, reaction has occurred in the carrier solution. Exposure of the crystal to low neutron doses after thorough de-gassing resulted in a high yield of radioactive phosphine, hypophosphite and phosphite on subsequent carrier analysis. It is claimed that this result accords with the theoretical expectation that, since the recoil energy of the phosphorus atom is too low for self-ionization to occur except at very high neutron energies, the phosphorus atom formed from the chloride ion would carry a $-3$ charge after the nuclear event. At high neutron doses, or if the sample was exposed to gamma radiation subsequent to pile irradiation, the proportion of radioactive phosphate in the products increased; this result is construed to indicate that the gamma component of the reactor irradiation is responsible for the conversion of phosphorus from the $-3$ to the $+5$ state as reflected in the product distribution. Additional experiments showed that the phosphorus activity could not be removed as the pentachloride, even by heating the crystal as high as 850°C., and this annealing treatment did not appreciably affect the amount of phosphate measured in solution. The last result appears to contradict the previous work of Süe and Caillat.[41] The range of $^{32}$P recoil in sodium chloride has been determined as $0{\cdot}5 \pm 0{\cdot}2\ \mu$ by Süe.[42]

It is convenient to divide the remaining discussion into parts dealing separately with inorganic and organic compounds of phosphorus.

## INORGANIC COMPOUNDS

### Phosphine

Electron impact measurements on phosphine in a mass spectrometer[43] have shown that $PH_3^+$, $PH_2^+$, $PH^+$ and $P^+$ ions can all be formed in varying abundance, depending on the ionizing energy of the electrons. The ionization potential of phosphine was determined to be $10{\cdot}0 \pm 0{\cdot}2$ ev. and the appearance potential of $PH_2^+$ corresponding to the dissociation process:

$$PH_3^+ \rightarrow PH_2^+ + H$$

was found to occur at $13{\cdot}9 \pm 0{\cdot}3$ ev. In the same investigation[43] two appearance potentials were observed for $PH^+$; the first at $12{\cdot}0 \pm 0{\cdot}3$ ev. corresponding to the dissociation:

$$PH_3^+ \rightarrow PH^+ + H_2$$

and a second located at 14·2 ev. is thought to arise from the more endothermic process:

$$PH_3^+ \rightarrow PH^+ + 2H$$

Some recent measurements by Stevenson[16] substantiate the ionization potential of phosphine as 10·1 ev., but the difference between this latter value and the appearance potential of $PH^+$ is given as 2·7 ev. which does not accord with the values quoted above. The appearance potential of the $P^+$ ion from phosphine was measured at $16{\cdot}7 \pm 1{\cdot}0$ ev. by Neuert and Clasen[44] and is thought to arise from the dissociation of the parent ion in the process:

$$PH_3^+ \rightarrow P^+ + H_2 + H$$

Stevenson[16] has discussed the use of mass spectrometric data to calculate the fragmentation pattern of parent ions for time intervals which are outside the range of observation, i.e., for less than $10^{-5}$ sec. after initial ionization, but which are of interest in radiation chemistry. By a treatment based on the quasi-equilibrium rate theory[45] of the origin of mass spectra, Stevenson has calculated[16] that the fraction of phosphine parent ions, $f_p$, which do not decompose to give $PH^+ + H_2$ after $10^{-10}$ sec. is 0·87. This calculation is valid for that region of ionizing electron energy (usually greater than 40 ev.) where $f_p$ is essentially constant. By comparison, the experimentally observed $f_p$ corresponding to a time of $10^{-5}$ sec. after initial ionization of phosphine is 0·38. Thus the usual mass spectrum pattern is not truly indicative of the ion distribution corresponding to the time before ion-molecule and collisional deactivation processes begin to intervene in the radiation chemistry of gases at appreciable pressures. Further aspects of this problem have recently been examined by Futrell for the case of propane.[46] It should be pointed out, however, that the statistical rate theory[45] in its present form appears to have distinct limitations in accounting for many aspects of ion-dissociation kinetics,[47] although it remains the only approach which has hitherto been developed. For the case of phosphine and small molecules, the theory[45] may be particularly unsuitable since the excited levels of $PH_3^+$ could well be discrete with low probabilities for rapid energy randomization as required by the model.

The only report[34] dealing with the macroscopic radiation chemistry of phosphine suggests that decomposition by reactor or gamma radiation occurs according to the overall equation:

$$PH_3 \rightarrow P + \tfrac{3}{2}H_2$$

There was no evidence for diphosphine, $P_2H_4$, or a polymer of the form $(PH)_x$ in the irradiation products. Attempts[34] to initiate the formation of phosphine by the irradiation of phosphorus and hydrogen gas were unsuccessful. In contrast to the dearth of experimental information on the mechanism of phosphine decomposition by radiolysis, the photochemical reaction has received detailed attention. Melville[48-9] studied the direct photolysis and found a quantum yield of 0·5 which increased with the diameter of the reaction vessel; additional experiments on the photosensitized reaction showed that the decomposition could be inhibited by atomic, but not by molecular, hydrogen. In conformity with these results, the following mechanism was formulated:

$$\text{(a)}\qquad \begin{array}{l} PH_3 + h\nu \rightarrow PH_2 + H \\ PH_2 + H + \text{wall} \rightarrow PH_3 \\ H + H + \text{wall} \rightarrow H_2 \\ PH_2 + PH_2 \rightarrow P_2 + 2H_2 \end{array}$$

In a similar investigation,[50] the quantum yield for the decomposition of trideuterophosphine was shown to be 1·1 times that for phosphine and this difference was attributed to a change in the relative frequencies of the secondary reactions. As a supplement to this earlier and classical approach some recent work by Norrish and Oldershaw,[51] using the techniques of flash photolysis[6,52] and kinetic spectroscopy, has led to the direct spectroscopic identification of $PH_2$, PH, and $P_2$ as reaction intermediates and provides new insight into the detailed mechanism of the decomposition. This latter work is an elegant example of the use of modern methods to demonstrate the unequivocal existence of transient chemical species such as free radicals. The overall stoicheiometry of the reaction induced by flash photolysis agrees with the equation:

$$PH_3 \rightarrow P\,(\text{red}) + \tfrac{3}{2}H_2$$

Immediately after the discharge of a flash, a high concentration of radicals is generated in the reaction vessel and this results in the secondary reactions occurring homogeneously, whereas with conventional light sources the secondary reactions are probably heterogeneous in character. Following the primary act, two possible processes can be written to account for the formation of the PH radical:

$$\text{(b)}\qquad PH_2 + PH_2 \rightarrow PH_3 + PH$$

or

$$H + PH_2 \rightarrow H_2 + PH$$

If the latter reaction is predominant, the quantum yield would be expected to show no temperature dependence since the hydrogen atoms would be eliminated from the system before the secondary abstraction reaction:

$$H + PH_3 \rightarrow H_2 + PH_2$$

could occur. However, it was found that the yield of the reaction was reduced if phosphine was flash-irradiated in the presence of an inert diluent; these conditions correspond to a lower effective temperature for the above secondary reactions. Hence the reaction between $PH_2$ radicals is assumed to give PH, and the increase in yield with rising temperature is attributed to the reaction of H with $PH_3$. It is consistent with the above scheme that a reaction between two radicals would be expected to have a lower activation energy than a radical-molecule interaction. A mechanism for the homogeneous photolysis of phosphine at low temperatures is therefore represented adequately by the following reactions:

$$\begin{array}{ll} & PH_3 + h\nu \rightarrow PH_2 + H \\ \text{(b)} & 2PH_2 \rightarrow PH + PH_3 \\ \text{(c)} & 2PH \rightarrow P_2 + H_2 \\ & H + H + M\ (\text{or wall}) \rightarrow H_2 \end{array}$$

The quantum yield of 0·5 for the above sequence is identical with the value observed by Melville, but the mechanism differs from that proposed for the direct photolysis in the form of the reaction between $PH_2$ radicals; reaction (*b*) is conceptually much simpler than (*a*) and is thought to be more important in the gas phase although it is conceded that (*a*) may well occur on the walls and could therefore be important under the conditions used by Melville. The absence of $P_2H_4$ formation suggests that combination of $PH_2$ radicals does not occur as an alternative to (*b*). In the flash photolysis,[51] $P_2$ was produced in a vibrationally excited state ($\nu''=7$) with up to 15 kg.-cal. excess energy, but it is uncertain whether this excitation is produced in the chemical reaction (*c*) or by absorption from the 'tail' of the photoflash followed by fluorescence back to the upper vibrational levels of the ground state. Deactivation of the $P_2$ molecule from the upper levels is fairly rapid and the lifetime of $\nu''=0$ level of $P_2$ is estimated between 1 and 2 msec., indicating that several thousand collisions take place before dimerization occurs to form $P_4$ molecules. If inert gas is present, the phosphorus remains suspended in the gas phase for several minutes before the particles grow large enough to sediment as a deposit of red phosphorus on the bottom of the flask. When ammonia was present with phosphine during flash photolysis, the absorption spectrum of PN was subsequently observed. This result indicates that the probable reaction:

$$(d) \qquad PH + NH \rightarrow PN + H_2$$

must have an activation energy comparable with process (*c*); it follows that, since the N–H bond dissociation energy exceeds that of P–H, both reactions (*c*) and (*d*) occur with very low activation energy.

The oxidation of phosphine is a branched-chain reaction which occurs spontaneously with explosion between certain pressure limits. However, the reaction can be induced photochemically outside these limits and followed quantitatively.[50,53] By flash photolysis[54] the radicals $PH_2$, PH, OH and PO were identified in the reaction mixture and the decay of their absorption spectra with time was followed. The results of this work[54] suggest that $PH_2$ and OH act as chain carriers in the straight propagation reactions:

$$PH_2 + O_2 \rightarrow HPO + OH$$

followed by:

$$OH + PH_3 \rightarrow H_2O + PH_2$$

The radical PH is assumed to be generated less frequently by the reaction:

$$PH_2 + O_2 \rightarrow PH + HO_2$$

and to react subsequently with an oxygen molecule to form an oxygen atom:

$$PH + O_2 \rightarrow HPO + O$$

The oxygen atom is then responsible for chain branching according to the process:

$$PH_3 + O \rightarrow PH_2 + OH$$

According to this plausible scheme,[54] termination is effected at low pressures by the reaction of oxygen atoms with other free radicals at the wall and at high pressures by the loss of oxygen atoms due to combination with molecular oxygen to form ozone. The previous mechanisms[50,55] postulated for this reaction stressed the importance of HPO as the intermediate involved in chain branching.

## Phosphorus Halides

The distribution of ions formed by electron impact on phosphorus trichloride is known from the work of Kusch, Hustrulid and Tate[56]; their values for the appearance potentials of the fragment ions and relative ion intensities at an electron ionizing of 120 volts are tabulated below:

| Ions | Abundance (120 volts) | Appearance potential (ev.) |
|---|---|---|
| $PCl_3^+$ | 100 | 12·2 |
| $PCl_2^+$ | 182 | 12·5 |
| $PCl^+$ | 38 | 17·5 |
| $P^+$ | 36 | 22·1 |
| $PCl_2^{++}$ | 2·4 | |
| $PCl^{++}$ | 0·4 | |

Since the appearance potential of $PCl_2^+$ is only slightly greater than the ionization potential for $PCl_3$, the high intensity of $PCl_2^+$ in the above fragmentation pattern can be attributed to a low activation energy for the dissociation process:

$$PCl_3^+ \rightarrow PCl_2^+ + Cl$$

This evidence would appear to suggest that chlorine atoms may be readily formed in the gas-phase radiolysis of phosphorus trichloride.

A study[57] of the labelled chemical species formed by neutron irradiation of phosphorus trichloride indicated that 88% of the total $^{32}P$ was present as $^{32}PCl_3$, irrespective of the total neutron dose, irradiation temperature or physical state (liquid or gas) of the compound. This conclusion [57] was revised according to a later study [58] which showed that for shorter irradiation exposures of liquid phosphorus trichloride, the proportion of $^{32}P$ in combination as $^{32}PCl_3$ was significantly lower than the above result and increased with time of irradiation from 60 to 90%. This latter growth is postulated to be caused by a radiation-induced conversion of radioactive $P_2Cl_4$ to form $PCl_3$. According to this scheme, the $P_2Cl_4$ is presumably formed by the combination of $PCl_2$ fragments remaining after P–Cl bond rupture in the recoil of the $^{32}P$. No visual decomposition was noted after irradiation and the residual fraction of the $^{32}P$ activity was probably present as phosphorus oxychloride.

A corresponding study[59] of reactor-irradiated phosphorus oxychloride showed that the $^{32}P$ fraction of activity present as $PCl_3$ decreased from 60% at low doses to a value of less than 10% for long irradiation exposure. Concurrently, the activity formed as $POCl_3$ increased over the same dose interval from 30 to greater than 80%. The possibility of phosphorus exchange in the $POCl_3$–$PCl_3$ system was shown to be negligible under the prevailing distillation conditions. It was further established that the *G* values for a gamma-ray induced phosphorus exchange were about 2·4 and 1·5 for respective concentrations of 3·7 and 1·4% $PCl_3$ in $POCl_3$, but this contribution could not account for the amount of $^{32}PCl_3$ present in the irradiated $POCl_3$. The authors[59] conclude that the high fraction of $^{32}PCl_3$ formed initially in the sample implies that a minimum number of three atoms must, on average, be split away in the recoil process following the $^{31}P(n, \gamma)^{32}P$ reaction; they further suggest that a secondary radiation-induced reaction involving recoil processes from $Cl(n, \gamma)$ reactions is responsible for the conversion of $^{32}PCl_3$ to give $^{32}POCl_3$ as well as a high-boiling component, presumably $PCl_5$, which is also assumed to be subsequently transformed to $POCl_3$. It is clear from the foregoing account that further work is required to clarify the many uncertainties with regard to the individual processes that occur in the neutron irradiation of phosphorus chlorides.

The kinetics of the gamma radiation-induced exchange of phosphorus in the $PCl_3$–$POCl_3$ system[60] have been shown to be adequately represented by the equation:

$$M = k'bD + k''abD$$

where *M* refers to the concentration of phosphorus exchanged while *a* and *b* are the respective concentrations of $PCl_3$ and $POCl_3$, all in units of millimoles per gram of solution, and *D* is the absorbed dose. The constants $k'$ and $k''$ were found to be $3{\cdot}19 \times 10^{-10}$ rad$^{-1}$ and $4{\cdot}24 \times 10^{-11}$ gram m.-mole$^{-1}$ rad$^{-1}$, respectively (1 rad $= 6{\cdot}24 \times 10^{13}$ ev. g.$^{-1}$). The first term of the above equation is independent of the $PCl_3$ concentration and is thought to correspond to a mechanism involving an exchange process in which the $POCl_3$ undergoes P–O bond rupture and the oxygen atoms then recombine with a molecule of $PCl_3$. The second term describes a second-order reaction which is presumed to involve either an induced transfer of oxygen between weakly coupled $PCl_3$–$POCl_3$ dipoles or else the exchange of oxygen during a collision process between the two component molecules when one of them is excited. Neglecting the second term in the above equation, i.e., for low concentrations of $PCl_3$, the $G$ value for phosphorus exchange at low conversion is deduced to be *ca.* 2·0 in agreement with earlier observations.[59]

It is reported[61–2] that a mixture of dry hydrogen and $PCl_3$ when subjected to a silent electric discharge results in the formation of $P_2Cl_4$, together with a small yield of red phosphorus contaminated with white phosphorus. If a copper cathode is used in the discharge tube, copper phosphide, $Cu_3P$, is apparently deposited on the electrode. By exposing $PCl_3$ alone to the effect of a high voltage discharge between mercury electrodes,[63] $P_2Cl_4$ is again produced. As part of a study of the irradiation effects of high energy electrons on mixtures containing an inorganic halide and a hydrocarbon, Henglein[64] found that the major products from the use of $PCl_3$ and $POCl_3$ are organic phosphorus dichlorides and organic derivatives of dichlorophosphine oxides, respectively. The overall process can be represented by the elimination of hydrochloric acid from the reactants:

$$PCl_3 + RH \rightarrow RPCl_2 + HCl$$

It appears that this simple process accounts for up to half of the total amount of initial material which undergoes reaction, and that conversions of 20–30% can be attained at high irradiation dosage. This method of radiation synthesis is recommended as a convenient route to several compounds which have not been prepared by conventional methods. It is postulated[64] that these reactions involve the intermediate formation of 'hot' hydrogen and chlorine atoms, but chain processes are ruled out by the magnitude of the yields. Since we have already indicated that the loss of chlorine atoms from ionized $PCl_3$ molecules would be expected to occur with relative ease, it is reasonable to suppose that a chlorine atom then undergoes a hydrogen-atom abstraction reaction with the hydrocarbon leaving an organic free radical to couple with the $PCl_2$ fragment. The amounts of $P_2Cl_4$ and hydrocarbon dimers in the products were generally much less than the yield of $RPCl_2$ and it is concluded[64] that the reaction between $R\cdot$ and $PCl_2\cdot$ is favoured over the combination or disproportionation of identical radicals. The irradiation of pure $PCl_3$ does not produce a yellow product, presumably phosphorus, which is usually found in the irradiated halide–hydrocarbon mixture. It is suggested that the phosphorus is formed from the secondary decomposition of the $P_2Cl_4$. A mixture of *n*-heptane and $PCl_3$ was found to give a number of isomers corresponding to the formula $C_7H_{15}PCl_2$. *cyclo*Hexene reacts with $PCl_3$ under these conditions to form a mixture of 3- and 4-*cyclo*hexenyl phosphorus dichlorides, the 3-isomer predominating; this result accords with the view that these reactions are of a free-radical character since a chlorine atom would be expected to abstract a hydrogen atom preferentially from the allylic 3-position in *cyclo*hexene.

Another interesting application of the use of radiation for synthetic purposes is in the preparation of phosphonitrilic chloride derivatives. Spitsyn[65] and co-workers have irradiated the tetramer of phosphonitrilic chloride as a 5% solution in absolute butyl alcohol; after exposure to 0·06 Mev. electrons for an integral dose of $1{\cdot}5 \times 10^{22}$ ev. ml.$^{-1}$, the yield of butyl phosphonitrilic ester remaining after removal of the *n*-butyl alcohol was found to be equivalent to the conversion of 45% of the initial phosphonitrilic chloride. This yield corresponds to a $G$ value of 1·6 for the replacement of chlorine atoms, based on total energy absorption. Thus it appears that the substitution of chlorine atoms by organic radicals is a reaction of some generality in the irradiation of phosphorus halides with organic compounds. The radiation stabilities of some of the lower homologues of phosphonitrilic chloride have been examined[66] by measuring the amount of insoluble polymer and gaseous products formed on bombardment with 4 Mev. electrons. On exposure of the solid (m.p. 113·5°C.) cyclic trimer $(PNCl_2)_3$ to a dose of $10^9$ rad, the yields of insoluble product were 2·62% and 5·19% for irradiations carried out *in vacuo* and under 1 atmosphere of oxygen, respectively. The addition of 10% benzoquinone increased the polymer yield, for the same dose, to 27% for irradiation at −78°C., although the same concentration of additive had little effect at room temperature; it is suggested that benzoquinone may act by accelerating a radiation-induced ionic polymerization at low temperature. Whereas the insoluble polymer formed in the presence of oxygen had the properties of a rubber, a waxy solid was produced when benzoquinone was added. A mixture of cyclic polymers of mean mol. wt. corresponding to $(PNCl_2)_{12}$ showed a steady increase in viscosity up to $5 \times 10^8$ rad, but the linear $(PNCl_2)_n,PCl_5$ polymer gave insoluble rubbers for doses below $2{\cdot}5 \times 10^8$ rad. The yields of chlorine gas obtained also indicate that the linear material is more susceptible to radiation decomposition than the cyclic compounds. Only a small amount of nitrogen was produced in comparison with chlorine, except in the case of the cyclic $(PNCl_2)_{12}$ where the measured nitrogen yield was almost twice that due to chlorine. The infrared spectra of the irradiated $(PNCl_2)_{12}$ showed no change in the bands attributable to P–Cl and P=N, but some absorptions indicative of P–O–P and $\rangle$P–OH linkages were observed for the material irradiated in oxygen. These authors[66] attribute the greater radiation stability of the cyclic phosphonitrilic chlorides over the linear polymers to the aromatic character of the former class[67]; however, this view may have to be modified in the light of a recent conclusion[68] that the resonance stabilization of the phosphonitrilic chlorides is due primarily to localized three-centre $\pi$-bonds involving a discontinuity in overlap at each phosphorus atom because of the use of two separate *d*-orbitals by phosphorus in $\pi$-bonding.

## Phosphorus Oxyacids

The oxyacids of phosphorus have been the subject of many irradiation studies, particularly concerning the effects accompanying $^{32}P$ recoil in solid crystalline salts exposed to thermal neutrons. On the latter subject, the results obtained by different workers are often in marked disagreement, and it is suspected that some, at least, of the discrepancies are due to variations in the techniques employed for the preparation of samples and in the handling and subsequent analysis after irradiation. The early work of Libby[69] indicated that for neutron-irradiated inorganic orthophosphates, approximately half of the $^{32}P$ remains in the pentavalent state with the remainder as trivalent phosphorus and that the immediate chemical environment does not affect this ratio. A series of similar investigations[70–6] have reported hypophosphite, phosphite, hypophosphate and pyrophosphate as radioactive products in addition to the retention of $^{32}P$ as orthophosphate, but most of this work refers to samples irradiated in the presence of air and often containing water of crystallization. By contrast, Sellers, Sato and Strain[34] claim that the main radioactive product from the irradiation of anhydrous $Na_2HPO_4$ in vacuum is orthophosphate with only traces of elementary phosphorus and some unidentified products. In addition, it has been shown that the effect of $3 \times 10^8$ roentgen of gamma radiation produces a negligible effect on the distribution of radioactive products. In a further study of phosphoric acid and a large number of its salts,[77] it has been confirmed that only traces of reduced radioactive products can be detected according to the electro-chromatographic method of separation and that the bulk of the activity is due to orthophosphate. A small amount of active material that migrated more slowly than the orthophosphate was claimed to be a condensed phosphate with similar properties to an irradiation product derived[75] from $KH_2PO_4$; this same product was also detected in samples which had been irradiated with gamma rays alone to high doses. The formation of pyrophosphate from the neutron irradiation of $Na_2HPO_4$ in 'boron-free' glass containers has been shown[78] to be an artefact due to the overall heating of the container during irradiation; the latter effect was found to be proportional to the boron content of the containers and therefore is attributed to energy release in the $^{10}B(n, \alpha)^7Li$ nuclear reaction. Samples irradiated under the same conditions in polyethylene or quartz tubes did not yield pyrophosphate. In some ancillary experiments,[78] the thermal conversion of disodium acid phosphate to pyrophosphate was followed by the technique of differential thermal analysis and an endothermic reaction was observed to occur between 325° and 390°C. The absence of pyrophosphate in the neutron-irradiated phosphate is presented as evidence[77] that the energy dissipation in $^{32}P$ recoil is unable to heat the activated molecule, or those in its immediate environment, to the necessary reaction temperature for a sufficient period of time to enable condensation to proceed. It has been argued[79] that the tracks of recoiling atoms do in fact correspond to localized zones of transient high temperature, and thus it would be interesting to investigate other systems where thermal effects of this type could perhaps be of greater importance. A second conclusion adduced by Sato *et al.*[77] from their results is either that P–O bonds are not disrupted or that they recombine after disruption in a manner identical with their disposition in the original material. The latter explanation is considered unlikely since samples of various condensed phosphates, including pyrophosphates and metaphosphates, were all shown to produce radioactive forms identical with the starting material regardless of physical state, degree of condensation or molecular size.

Despite the evidence reviewed above, there have been some recent suggestions[80-1] that the absence of reduced products and pyrophosphates as revealed by the experiments of Sato *et al.*[34, 77-8] may have been due to annealing processes arising in the pile from thermal effects and the concomitant gamma radiation, or from the heating of the sample during separation by electrophoresis. Claridge and Maddock[80] report that the products of neutron irradiated ammonium and potassium dihydrogen phosphates can undergo appreciable annealing by a thermal treatment at about 100°C. and by ultra-violet or electron irradiation, with a substantial increase in the percentage of activity retained in both total phosphate and orthophosphate fractions. Yoshihara and Yokoshima[81] irradiated a wide variety of orthophosphates and found large amounts of activity as phosphite, hypophosphite, pyrophosphate and higher condensed phosphates. The retention of activity in the parent phosphate appears to be greater, while the fraction of activity in the form of combined phosphite and hypophosphite is generally smaller, for hydrated relative to anhydrous salts. In contrast to the conclusions mentioned earlier, the latter authors suggest that local high temperatures are produced during $^{32}P$ recoil[79] and that this explains the formation of radioactive pyrophosphate and higher polyphosphates, including polymetaphosphates, $(MPO_3)_n$. It is clear that the points in dispute regarding $^{32}P$ recoil effects in organic phosphates can be resolved only by additional experiments designed to eliminate the uncertainties in regard to irradiation conditions and methods of analysis.

The neutron irradiation of disodium hydrogen phosphite and sodium dihydrogen hypophosphite under anhydrous conditions *in vacuo* has been shown[34] to result in about 50% retention of the $^{32}P$ in the original salt. Both hypophosphite and phosphate are formed from phosphite, and phosphite together with phosphate are products from hypophosphite. From the results on these salts using pile and gamma radiation separately, it appears that gamma rays alone induce similar chemical changes to those encountered in the formation of the $^{32}P$ recoil products. However, the gamma component of pile radiation cannot solely account for the changes in chemical constitution of the radioactive products.

Although there is a conflict of evidence on the chemical stability of solid inorganic phosphates subjected to the effects of thermal neutron capture, the extensive work of Cottin, Haïssinsky and Lefort[82-5] on the gamma- and alpha-ray irradiation of the inorganic phosphite–phosphate system in aqueous solution leaves little doubt that the phosphate ion is not reduced in either aerated or deaerated systems. It should also be mentioned that the use of relatively large concentrations of phosphate ions in the preparation of aqueous buffer solutions for the irradiation of solute systems has been practised[86] without, apparently, affecting the primary radiolysis of water to any significant extent. In this respect, the behaviour of phosphate appears to parallel that

**Refs. p. 1389**

of sulphate, and it would appear that these anions are highly stable both to the direct absorption of energy[87] and to the radiolysis products of water. A general description of the radiation chemistry of aqueous solutions[88-9] is outside the scope of this section, but it is pertinent to discuss the main features of the radiation-induced oxidation of phosphite ion in dilute solution,[82-5] Cottin[85] has established that phosphite ions are completely oxidized to phosphate under all irradiation conditions, both in the presence and in the absence of oxygen in solution. Thus there is no evidence for a radiation-induced equilibrium between phosphite and phosphate ions. In irradiations with 10 Kev. *X*-rays or $^{60}$Co gamma-rays the oxidation yield in evacuated solutions is equivalent to the hydrogen gas evolved, but the magnitude of this yield depends both on the pH of the solution and the initial phosphite concentration. For a concentration of $10^{-3}$ M. phosphite, the oxidation yield ($G$) is 3·15 at a pH of 0·1 but declines to 1·8 at a pH of 7·7. The oxidation yield at constant pH appears to reach the maximum value at a concentration of $2 \times 10^{-3}$ M. phosphite with a $G$ yield of 3·75 in 0·8 N. $H_2SO_4$ solution (pH$\simeq$0·1). The last oxidation yield cannot be attributed solely to the effect of the OH radical, since two OH species must be involved in the oxidation of a single phosphite ion according to the overall equation:

$$H_2PO_3^- + 2OH \rightarrow H_2PO_4^- + H_2O$$

and this process alone would imply the formation of 7·5 OH radicals per 100 ev., which is more than twice the known value of $G(OH) \simeq 3{\cdot}2$. Hence it is inferred that H atoms are also able to oxidize phosphite according to the equation:

$$H + H_2PO_3^- \rightarrow H_2 + HPO_3^-$$

this represents an exothermic process since the bond dissociation energy of H–H (103 kg.-cal./mole) exceeds that of P–H (63 kg.-cal./mole). A combination of oxidation steps provided by OH radicals and H atoms can therefore account for the equivalence of hydrogen gas to the oxidation yield, and the mechanism is postulated to proceed through a single tetravalent intermediate ($H_2PO_3$, $HPO_3^-$ or $PO_3^{2-}$):

$$\begin{gathered} H_2PO_3^- + OH \rightarrow HPO_3^- + H_2O \\ H_2PO_3^- + H \rightarrow HPO_3^- + H_2 \\ 2HPO_3^- + H_2O \rightarrow H_2PO_3^- + H_2PO_4^- \end{gathered}$$

In the presence of added hydrogen peroxide, the phosphate yield is enhanced owing to the reaction:

$$HPO_3^- + H_2O_2 \rightarrow H_2PO_4^- + OH$$

When oxygen is present, the initial oxidation yield ($G$) reaches a maximum at pH 3·0 and is about 30 at pH 2·15 for $10^{-3}$ M. phosphorous acid. The consumption of 1 molecule of oxygen corresponds, at high phosphite ion concentration, to the oxidation of two phosphite ions. A mechanism consistent with the results involves the following reactions:

$$\begin{array}{ll} & H_2O \xrightarrow{O_2} HO_2 + OH \\ & H_3PO_3 \rightleftharpoons H_2PO_3^- + H^+ \\ (1) & H_2PO_3^- + OH \rightarrow HPO_3^- + H_2O \\ (2) & HPO_3^- + O_2 \rightarrow HPO_3 + O_2^- \\ (3) & HPO_3 + H_2O \rightarrow H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \\ (4) & H^+ + O_2^- \rightleftharpoons HO_2 \\ (5) & H_2PO_3^- + HO_2 \rightarrow H_2PO_4^- + OH \end{array}$$

The propagation steps in this chain oxidation involve the electron transfer reaction (2) followed by (4) and (5); termination is assumed to occur by inter-radical reactions as in (6) and (7).

$$\begin{array}{ll} (6) & HPO_3^- + OH \rightarrow H_2PO_4^- \\ (7) & OH + HO_2 \rightarrow H_2O + O_2 \end{array}$$

The dependence of the yield on pH is explained qualitatively in terms of the ionization equilibria involving $H_3PO_3$ and $HO_2$; both these latter species are largely dissociated in neutral solution where reaction (5) takes the form:

$$H_2PO_3^- + O_2^- \rightarrow HPO_4^{2-} + OH$$

and would involve strong electrostatic repulsion between the reacting entities. Thus chain propagation by this route is impeded and a lower yield obtains. At low phosphite concentration the relationship of one oxygen molecule consumed per two phosphite ions oxidized breaks down and this is explained in terms of the increased importance of inter-radical reactions (6) and (7) over radical-solute processes (1) and (5). The action of polonium α-rays on this system results in much lower $G$ yields for phosphite oxidation relative to the values obtained for gamma irradiation under corresponding conditions. In deaerated solution the sum of $G_{(\text{phosphate})} + G_{H_2O_2} + 2G_{O_2}$, corresponding to a total oxidation yield for the system, is constant (*ca.* 1·7) and agrees with $G_{H_2}$ over the entire concentration range from $10^{-4}$ to $10^{-1}$ M. phosphite ion in 0·8 N. $H_2SO_4$. While $G_{O_2}$ assumes a mean value of 0·45 almost independent of phosphite concentration, $G_{H_2O_2}$ (0·47) exceeds $G_{(\text{phosphate})}$ (0·19) at $2 \times 10^{-4}$ M. phosphite but at a higher solute concentration, ($5 \times 10^{-3}$ M.), $G_{H_2O_2}$ is reduced to zero and $G_{(\text{phosphate})}$ becomes 0·79. When 0·8 N. $H_2SO_4$ is irradiated in the absence of phosphite, $G_{H_2} = G_{H_2O_2} + 2G_{O_2} = 1{\cdot}75$.

These findings are interpreted[90] to mean that intra-track OH radical reactions yielding $O_2$ are unaffected even at high phosphite ion concentrations. The increase in $G_{(\text{phosphate})}$ with solute concentration would appear to be due to an increased efficiency of the scavenging reaction:

$$H_2PO_3^- + OH \rightarrow HPO_3^- + H_2O$$

augmented by the attack of $HPO_3^-$ on the 'molecular yield' of $H_2O_2$ according to the process:

$$HPO_3^- + H_2O_2 \rightarrow H_2PO_4^- + OH$$

Confirmation of the latter step is afforded by the observation of an enhanced phosphate yield ($G = 1{\cdot}6$) and complete removal of $H_2O_2$ on the irradiation of a $5 \times 10^{-3}$ M. phosphite solution containing added $3 \times 10^{-4}$ M. $H_2O_2$. In the presence of oxygen, phosphite concentrations exceeding $10^{-2}$ M. are necessary to attain oxidation yields indicative of a chain mechanism. This result is attributed to the effect of the high OH radical concentration in the α-ray track favouring the reaction of OH with $HPO_3^-$ immediately after formation of the latter:

$$OH + HPO_3^- \rightarrow H_2PO_4^-$$

thus decreasing the probability of the electron transfer step:

$$HPO_3^- + O_2 \rightarrow HPO_3 + O_2^-$$

previously postulated as the initial reaction in the gamma-induced chain oxidation.

The irradiation of aqueous phosphoric acid at 77°K. results in the formation of trapped atomic hydrogen which has been identified by electron spin resonance.[91] By comparison, atomic hydrogen is produced in irradiated ice[92] only at much lower temperatures, *ca.* 4°K., and disappears on warming much below 77°K. Thus it is evident that solid aqueous phosphoric acid constitutes a better stabilizing medium for atomic hydrogen than ice; aqueous perchloric and sulphuric acids behave similarly to phosphoric acid in this respect. It is also found [93] that the yields of atomic hydrogen are greater when the aqueous acid is irradiated in the glassy as compared with the crystalline state over the entire range of acid composition. The amount of molecular hydrogen evolved on warming the crystalline aqueous $H_3PO_4$ to the melting point is in good agreement with the yield of atomic hydrogen as determined by the paramagnetic resonance method; for the irradiated glass, the yield of atomic hydrogen exceeds that due to liberated hydrogen. The maximum initial yields for aqueous phosphoric acid are attained at a mole fraction of $H_3PO_4 \simeq 0{\cdot}2$; $G$(H) values of 0·6 and 1·0 are recorded for the crystalline and glassy states respectively whereas $G(H_2)$ is about 0·30, almost independent of state. An important conclusion derived from this work is that atomic hydrogen reacts preferentially by atomic combination in these systems rather than with the other paramagnetic species present; this is confirmed by the observed persistence of paramagnetic resonance after the characteristic spectrum of atomic H has disappeared on warming the sample to a temperature still considerably below the melting point.

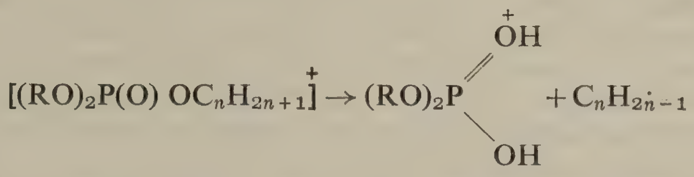
## ORGANIC PHOSPHORUS COMPOUNDS

Numerous studies of the irradiation of organophosphorus compounds have been motivated by the technological needs of the nuclear energy industry. One compound which has been studied repeatedly is tri-*n*-butyl phosphate (TBP) since it finds application as a solvent for the processing of nuclear fuels. There is a general consensus of agreement that *di-* and *mono-n*-butyl phosphoric acids are formed together with gaseous and polymeric products; the yields recorded by different investigators are shown in Table I.

*Table I.—G-values for Radiolysis of Tri-n-butyl Phosphate*

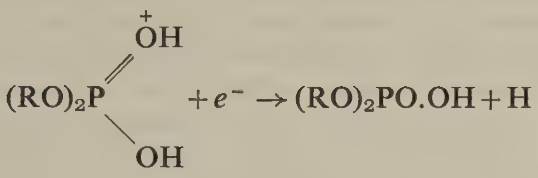
| Author | Radiation used | Dibutyl phosphate DBP | Monobutyl phosphate MBP | $H_2$ | $CH_4$ | $C_2$ | $C_3+C_4$ |
|---|---|---|---|---|---|---|---|
| Williams, Wilkinson and Rigg[94]<br>Wilkinson and Williams[95] | 1·25 Mev. electrons | 1·52 | 0·12 | 1·11 | 0·05 | 0·24 | 0·45 |
| Burger and McClanahan[96] | Co–60 gamma | 1·7–1·8 | 0·3 | | | | |
| Wagner, Kinderman, and Towle[97] | 1 Mev. electrons | 2·25–1·37 | 0·39–0·03 | 1·59 | 0·07 | 0·13 | 0·75 |
| Burr[98] | 1·66 Mev. electrons | 2·44 | 0·14 | 1·73 | 0·07 | 0·18 | 0·65 |

Burger and McClanahan[96] claim that in addition to the products listed, *n*-butyl alcohol is formed, but it could not be detected as an irradiation product from the radiolysis of TBP saturated with water.[94] It is interesting that the presence of water in the TBP reduces the yield of acidic products,[94, 96] and there is no evidence that the mechanism of decomposition by radiolysis is related to the mode of hydrolysis. In this respect, it is pertinent to mention that studies[99] of the chemical stability of TBP in nitrate and chloride solutions indicate that the acid-catalyzed reaction is not a hydrolysis but involves dealkylation; similarly, the thermal decomposition[100] occurs with olefin elimination and is catalyzed by acids. Burr has suggested[98] that the mechanism of TBP radiolysis can be interpreted on parallel lines to the radiation chemistry of ethanol[101] and other alcohols, according to which the primary process would be the rupture of a C–H bond at one of the carbon atoms linked to the oxygen in the phosphate group. Another view[95] is based on recent mass-spectral work[102–3] which has demonstrated that parent organic phosphate ions, in the gas phase, can undergo facile rearrangement with the fragmentation of one, two or all three alkyl chains. An extrapolation of the last results to account for the radiolysis products in the liquid phase requires the fragmentation pattern to be modified so that only primary decomposition processes involving the rupture of one alkyl chain are predominant; it has been argued[95] that this is a reasonable assumption and that the criterion of exothermicity determines whether parent ions can undergo dissociation in the liquid phase before neutralization[15]:



$$[(RO)_2P(O)\,OC_nH_{2n+1}]^{+} \rightarrow (RO)_2P(\overset{+}{O}H)(OH) + C_nH_{2\dot{n}-1}$$

The neutralization of the fragment ion is considered to proceed by removal of a proton with the formation of a dialkyl phosphate molecule and a hydrogen atom:



$$(RO)_2P(\overset{+}{O}H)(OH) + e^{-} \rightarrow (RO)_2PO.OH + H$$

Because of the short lifetime, *ca.* $10^{-13}$ sec., of an ion in the liquid phase, the diffusion distance of the radical $C_nH_{2n-1}$ in the interval between rearrangement and neutralization would be small so that both $C_nH_{2n-1}$ and H are formed in close proximity according to this model, thus favouring their combination. Hence the products of the above reactions may be amended to dialkyl phosphate and olefin. In an extended study[95] the *G* yields of dialkyl phosphoric acids have been shown to decrease in the series trimethyl to tripentyl phosphate, whereas *G* for hydrogen gas formation increases with molecular weight. These results are interpreted[95] on the premise that the parent ion can either undergo dissociation and rearrangement as indicated above or else react with a neighbouring molecule to form a dimer by loss of molecular hydrogen. Since the dimerization or cross-linking reaction is well known in the radiation chemistry of linear alkanes, it is reasoned that this type of process would be expected to attain greater importance as the alkyl groups increase in size. It should be added that neither oxygen gas nor pyrophosphates have been found as products of the gamma- or fast electron-radiolysis of these organic esters of orthophosphoric acids; this lends further support to the view that the phosphate group is inherently stable to irradiation.

It is interesting to compare the above information with some results which have been obtained for the distribution of $^{32}P$ in TBP samples exposed to neutron irradiation.[104] At low neutron beam intensities, it appears that only a small amount (5·5%) of the total activity remains in the parent molecule and appreciable fractions are due to DBP (22–28%), MBP (33%), and inorganic phosphorus compounds (26–36%) soluble in water; the last fraction consists mainly of orthophosphate and orthophosphite. This proportion of $^{32}P$ activity in the aqueous phase is similar to that observed in the neutron irradiation of triphenyl phosphate in benzene[105] where 40% of the induced activity dissolved in water. On the other hand, when TBP is irradiated at high neutron fluxes[104] the $^{32}P$ is retained preferentially (59%) as radioactive TBP with considerably smaller fractions in the form of MBP and in the aqueous extract, although the DBP fraction remains appreciably similar (24%) to that encountered at lower neutron intensities. The possibility that isotopic exchange affects the distribution of yields is ruled out on account of previous work. Some calculations[104] based on a stochastic procedure[106] for determining the probability of escape by a recoiling atom from the parent molecule suggest that only 3% of $^{32}P$ atoms remain as originally bound. Hence, it is concluded that the high yield of $TB^{32}P$ must be the result of recombination processes involving radical fragments and is not due to primary retention; the results are held to be inconsistent with the 'billiard-ball' mechanism advanced by Libby.[107]

The chemical state of $^{32}P$ in neutron-irradiated phosphorus compounds has been explored in a number of other systems,[108-10] but it is almost impossible to obtain definitive evidence in condensed systems to decide between the alternatives of primary retention or recombination to explain the occurrence of activity in the parent molecule. However, a recent study by Halmann[111] has succeeded in clarifying the processes following thermal neutron capture in gaseous trimethylphosphine. Irradiation at pressures of about 100 mm. was shown to result in the formation of *ca.* 3% $^{32}P(CH_3)_3$ compared to 13·7% $^{32}PH_3$, 4·9% $^{32}PH_2(CH_3)$, and 0·8% $^{32}PH(CH_3)_2$; the remainder (77·7%) of the $^{32}P$ was deposited on the walls of the vessel. As the initial pressure was decreased in these experiments, the fraction of $^{32}P$ appearing in the parent compound was reduced still further until it represented less than 0·4% of the total activity at a pressure of 1·8 mm. In order to decide whether this effect is the result of a decrease in the probability of recombination at lower pressures or is due to a greater likelihood of disruption owing to the greater mean free path of the recoiling molecule, further experiments were performed with low partial pressures of trimethylphosphine in the presence of 50 mm. of added argon. The results indicated negligible retention, which suggests that moderation of the activated molecule by energy transfer in collisions is a negligible factor. Thus this evidence supports the recombination theory to explain retention in gaseous systems.

In addition to TBP, many other organophosphorus compounds have been examined as possible extraction solvents for the processing of radioactive materials, and an overall assessment of their potential value must include some consideration of radiation stability. In this connection, it has been shown[97, 112] that di-*sec*-butyl phenyl phosphonate and tri-*n*-octylphosphine oxide are slightly more resistant to fast electron radiation than TBP as judged by criteria of gas and acid production. It has been reported[113] that, in the presence of air, tri-*iso*propyl phosphite labelled with $^{32}P$ undergoes appreciable oxidation, whereas unlabelled material is unaffected under the same conditions. Some mass spectroscopic data have been recorded[114] for the cyclic dimethylphosphino-borine trimer, $((CH_3)_2PBH_2)_3$. It is interesting that the most abundant ion in the 70-volt spectrum is $B(CH_3)_2^+$ which must be formed by a rather extensive rearrangement process. This ion has the high appearance potential of 20 ev., so it is somewhat surprising to find it present in such high intensity even at an electron ionizing energy of 70 ev. The thermal decomposition of the trimer at 510°C. also results in the migration of methyl groups to boron with the eventual formation of methyl substituted boranes and of elementary phosphorus.

Considerable effort has been devoted over the past decade to the study of irradiation effects on biologically important substances, many of which contain phosphorus in the molecular structure. In particular, the nucleic acids have been widely investigated under varying conditions of irradiation exposure. A recent review[115] summarizes much of the information which has been obtained. It is worthy of mention that the use of physical methods has contributed greatly to the general understanding of irradiation effects on macromolecules, and an elegant example is the deduction[116] from viscosity and light-scattering measurements that two irradiation-induced breaks must occur close together in deoxyribonucleic acid (DNA) to effect scission; this finding concurs with the Watson–Crick model for DNA involving a two-stranded polynucleotide structure. The complementary investigations of chemical changes have been centred mainly on aqueous solutions where the effects are 'indirect' and proceed through the radical products from the radiolysis of water. Scholes, Weiss and their collaborators[117] have presented evidence for reactivity at various positions in the nucleic acid structure leading to breakage of the nucleotide chain, hydroperoxide formation in the presence of oxygen, deamination of the base, and ring fission. Inorganic phosphate is reported to be produced in low yield both directly during irradiation and in a subsequent post-irradiation reaction. It is clear that for such a complex molecule, the mechanism of radical attack is non-selective and that the overall process is one of great chemical complexity. Since the diester from phosphoric acid and sugar hydroxyl groups constitutes the essential linkage in the nucleic acid chain, it is of related interest to examine the irradiation of simpler phosphate esters and a few investigations have been reported along these lines. Butler and

Conway[118] have studied the kinetics of inorganic phosphate formation in the photolysis of aqueous solutions of mono-, di- and tri-ethyl phosphates containing hydrogen peroxide. The yield of inorganic phosphate from mono-ethyl phosphate varies linearly with time of irradiation, but the corresponding curves for di- and tri-ethyl phosphate show much smaller yields per unit time which increase slowly as the irradiation proceeds. These results are explicable on the postulate that the reaction is due to a cleavage of the alkyl chain at the carbon atom linked to the phosphate group, which in the case of the mono-alkyl ester leads to direct phosphate ejection. The liberation of free phosphate from the di- and tri-esters is represented as the net result of two and three consecutive processes, respectively. Acetaldehyde and formaldehyde are formed from mono-ethyl phosphate, but there is no evidence for labile esters which degrade subsequent to the irradiation. All the facts are consistent with a simple scheme whereby some of the primarily formed OH radicals abstract hydrogen atoms from the alkyl group(s) to produce organic radicals, and the latter combine with more OH species to form an unstable product which breaks down readily to give an aldehyde and inorganic phosphate:

$$CH_3CH_2OPO_3H_2 + OH \rightarrow CH_3\dot{C}HOPO_3H_2 + H_2O$$
$$CH_3\dot{C}HOPO_3H_2 + OH \rightarrow CH_3CH(OH)OPO_3H_2 \rightarrow CH_3CHO + H_3PO_4$$

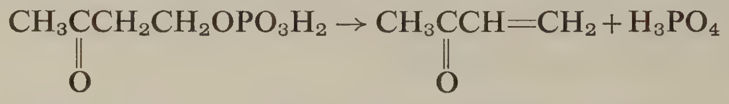
Concerning the effects of ionizing radiation on aqueous solutions of organic solutes, it is generally found that the presence of oxygen in the solution during irradiation modifies the results both quantitatively and qualitatively. This behaviour is particularly evident for the esters of phosphoric acid, and can be attributed to the combination of molecular oxygen with organic radicals $R\cdot$ to form peroxy-intermediates $RO\cdot_2$ which undergo subsequent reactions (*vide infra*). Thus Scholes and Weiss[119] have shown that acetyl phosphate is formed from the irradiation of mono-ethyl phosphate solutions containing oxygen, but only inorganic phosphate is produced *in vacuo*.[119–120] Further work[120–1] on the irradiation of aqueous solutions of the mono-alkyl phosphoric acids in the series from methyl to *n*-pentyl has contributed information as to the distribution of radical attack on an extended alkyl chain. In the absence of oxygen, only inorganic phosphate is formed from each of the esters examined, and the *G* values for irradiation at pH 8 decrease from 1·1 for the methyl ester to 0·3 for both *n*-butyl and *n*-pentyl phosphate. These results were found to be less reproducible than those obtained in oxygenated solution and also showed some dependence on dose rate.[121] The yields obtained at pH 8 in the presence of oxygen[120–1] are given in Table II; these values are independent of solute concentration above $10^{-3}$ molar.

*Table II.—Product Yields from the Irradiation of Monoalkyl Phosphates*
($10^{-3}$ M. solutions at pH 8)

| Solute | *G* Inorganic phosphate | *G* Acyl phosphate | *G* Labile phosphate(a) | *G* Acid | *G* Aldehyde | $G_i$ Total hydro-peroxide | $G_i$ $H_2O_2$ |
|---|---|---|---|---|---|---|---|
| Methyl | 2·8 | 0 | 0 | 2·4(b) | 0·4 | 3·3 | 3·3 |
| Ethyl | 1·0 | 1·3 | 0 | — | 0·85 | 2·9 | 2·9 |
| *n*-Propyl | 1·0 | 0·35 | 0·2 | — | 0·8 | 2·8 | 1·6 |
| *n*-Butyl | 1·0 | 0·15 | 0·7 | — | 0·8 | 2·8 | 1·4 |
| *n*-Pentyl | 0·9 | *ca.* 0·1 | 0·2 | — | 0·75 | 2·7 | 1·2 |

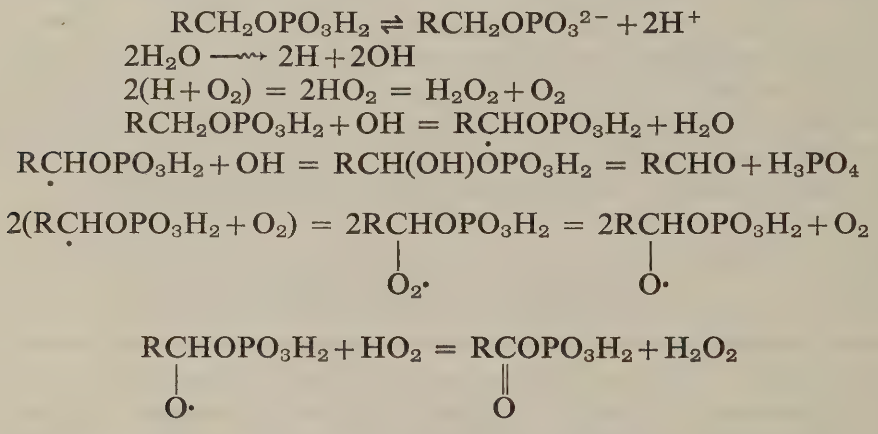
*i* Refers to initial yields.
(a) Refers to inorganic phosphate liberated after irradiation.
(b) Refers to formic acid.

The results for methyl phosphate appear anomalous in regard to the absence of acyl phosphate, but no compound corresponding to formyl phosphate appears to be known and in view of the increase in lability of acyl phosphates with decreasing length of alkyl chain, it is inferred that such a product would hydrolyze rapidly under the mildest conditions. A high yield of formic acid supports this contention. Except for methyl phosphate, the yields of inorganic phosphate and aldehyde appear to be comparable for each solute. The aldehyde was identified as having the same number of carbon atoms as the alkyl group from which it was derived, and it is reasonable to suppose that aldehyde and inorganic phosphate are formed in a common process through an intermediate similar to that postulated to account for the reaction of OH radicals with ethyl phosphate.[118] The yield of labile phosphate is taken to represent the subsequent breakdown of ketophosphates formed by radical attack at $\beta$- or $\gamma$-carbon atoms. Evidence on this point is provided by the marked catalysis of the post-irradiation effect for butyl phosphate by added alkali, which indicates that the process is mainly an elimination reaction rather than a hydrolysis[121]:



$$CH_3\underset{\underset{O}{\|}}{C}CH_2CH_2OPO_3H_2 \rightarrow CH_3\underset{\underset{O}{\|}}{C}CH{=}CH_2 + H_3PO_4$$

Since no after-effect of any type was observed for irradiated ethyl phosphate, it is surmised that initial radical attack occurs predominantly at the $\alpha$-carbon atom leading to acetyl phosphate and inorganic phosphate. It is also consistent that the $G$ values for inorganic + acyl phosphate derived from methyl and ethyl phosphate are not appreciably less than $G_R$ (radical yield) = *ca.* 3·2. In the case of the larger alkyl groups, application of the same criteria as above leads to the conclusion that $\rangle CH_2$ groups remote from the phosphate group are attacked by the primary radicals in irradiated water. The tabulated results refer to the natural pH (7·8) of a solution of the sodium or barium salt; variation of pH showed that maximum yields were attained at this latter value except for the case of ethyl phosphate where higher yields were observed in acid solutions. A mechanism reasonably consistent with the results for methyl and ethyl phosphate is given by the following scheme of reactions[121]:



$$RCH_2OPO_3H_2 \rightleftharpoons RCH_2OPO_3^{2-} + 2H^+$$
$$2H_2O \rightsquigarrow 2H + 2OH$$
$$2(H + O_2) = 2HO_2 = H_2O_2 + O_2$$
$$RCH_2OPO_3H_2 + OH = R\underset{\bullet}{C}HOPO_3H_2 + H_2O$$
$$R\underset{\bullet}{C}HOPO_3H_2 + OH = RCH(OH)OPO_3H_2 = RCHO + H_3PO_4$$
$$2(R\underset{\bullet}{C}HOPO_3H_2 + O_2) = 2R\underset{\underset{O_2\cdot}{|}}{C}HOPO_3H_2 = 2R\underset{\underset{O\cdot}{|}}{C}HOPO_3H_2 + O_2$$
$$R\underset{\underset{O\cdot}{|}}{C}HOPO_3H_2 + HO_2 = R\underset{\underset{O}{\|}}{C}OPO_3H_2 + H_2O_2$$

An interesting effect[122] has been observed on irradiation of oxygenated solutions of methyl or ethyl phosphoric acid containing added *ca.* $10^{-3}$ M. hydrogen peroxide. At pH 8 and below, the yield of total phosphate (inorganic + acyl) liberated is enhanced over the value given in the absence of $H_2O_2$, but at pH 12 the opposite result is found. While the increase in yield can be readily explained in terms of a contribution due to reactions of the form:

$$R\underset{\bullet}{C}HOPO_3H_2 + H_2O_2 = RCH(OH)OPO_3H_2 + OH$$

the reduced yield at high pH can only be rationalized on the basis of a competition between $H_2O_2$ and the alkyl phosphate for OH radicals. Since there is evidence[123] that OH is largely dissociated to $O^-$ at a pH exceeding 10, it is suggested that electrostatic repulsion between $O^-$ and the ionized alkyl phosphate anion hinders the process of hydrogen abstraction in this instance, thus allowing other reactions of $O^-$ radicals to compete more favourably, e.g.,

$$O^- + H_2O_2 \rightarrow H_2O + O_2^-$$
$$(\text{cf. } OH + H_2O_2 \rightarrow H_2O + HO_2)$$

The action of 200 kv. *X*-rays on aqueous solutions of α- and β-glycerophosphates has also been shown[124] to result in attack by OH radicals on the carbon atom linked to the phosphate and on neighbouring carbon atoms. In this case the $\rangle CH(OH)$ group is susceptible to oxidation by OH radicals and $\rangle C{=}O$ groups are formed even in the absence of oxygen. As a result, dihydroxyacetone phosphate is formed in addition to inorganic phosphate from α-glycerophosphate and although the presence of oxygen is not essential, higher yields of dihydroxyacetone phosphate obtain in aerated solution. Dihydroxyacetone phosphate is labile in alkaline solution and this is attributed to an elimination rather than a hydrolytic reaction. One of the main products from the irradiation of β-glycerophosphate is a phosphate ester labile to acid hydrolysis at high temperature. Organic hydroperoxides were not detected and therefore must be unstable if they are formed. The yields of the various products depend on solute concentration and pH. It is clear that the radiation chemistry of phosphorus oxyacids and their derivatives in aqueous solution is much influenced by the ionic form of the solute.

This section is concluded with a brief reference to the role of phosphorus compounds in photosynthesis. While it has long been recognized that esters of phosphoric acid participate as essential intermediates in many biological processes,[125] considerable interest is attached to the recent discovery by Arnon and co-workers[126] and by Frenkel[127] of the cyclic photosynthetic phosphorylation of adenosine-diphosphate(ADP) using isolated chloroplasts. Among the catalytic substances necessary for the reaction to proceed are magnesium ions and a suitable redox co-factor:

$$ADP^{3-} + HPO_4^{2-} + H^+ \xrightarrow[\text{chloroplasts}]{h\nu} ATP^{4-} + H_2O$$

It is thought that this reaction yields the ATP necessary to provide the 'driving force' for the reduction of carbon dioxide in the photosynthetic process, and it could therefore be regarded as the primary chemical reaction in photosynthesis.[128] Recent observations also indicate that a relation exists between photophosphorylation and the Hill reaction.[129] This refers to the process whereby oxygen gas is evolved from the irradiation of isolated chloroplasts in solutions containing a suitable oxidant which can function as a hydrogen atom or electron acceptor, e.g.,

$$2H_2O + 4Fe(CN)_6^{3-} \rightarrow O_2 + 4H^+ + 4Fe(CN)_6^{4-}$$

It has been claimed that the rate of the Hill reaction for isolated chloroplasts is stimulated by concomitant photophosphorylation but there is some dispute as to the findings.[130] The effect of β-radiation on chloroplasts has been shown[131] to affect their efficiency in both photophosphorylation and Hill reactions. A dose of 130,000 rad resulted in a 50% reduction of the rate of photophosphorylation, but a higher dose (530,000 rad) was necessary to effect the same decrease in the rate of the Hill reaction.

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## SECTION XXXIX

# BIOLOGICAL ASPECTS OF PHOSPHORUS

BY F. CALL

## INTRODUCTION

PHOSPHORUS is an element which appears to be essential to life. The element has been found in all forms of life in which it has been sought and it is believed that the life processes which occur on this earth would be impossible without phosphorus. The overriding importance of phosphorus appears to be its function as a key element in energy processes in living cells. Thus in all living cells which have been investigated phosphorus compounds have been found to be connected with the formation, conversion, transfer and storage of chemical energy. By simple structural changes in phosphorus esters carried out at normal temperatures by enzymes certain C–OP bonds become converted into 'high energy' bonds which are able to be transferred to other carbon compounds for synthetic or other purposes or to still other compounds which are able to store the 'energy rich' bond as a reserve until required. Much of this fascinating aspect of biochemistry is unfortunately beyond the scope of this review.

The very large number of literature references necessitates rigorous selection and only a representative sample can be discussed here, sufficient, however, to underline the important role that phosphorus plays in life processes.

The subject is reviewed under the following headings:

1. Phosphorus and Food.
2. Phosphorus and Micro-organisms.
3. Phosphorus and Plant Growth.
    - (i) Occurrence and Distribution of Phosphorus in Soils.
    - (ii) Availability of Phosphorus in Soils.
    - (iii) Phosphorus as a Fertilizer.
    - (iv) Deficiency of Phosphorus in Plants.
    - (v) Uptake of Phosphorus by Plants.
    - (vi) Metabolism of Phosphorus.
4. Phosphorus and Aquatic organisms.
5. Phosphorus and Invertebrates.
    - (i) Insects.
    - (ii) Helminths.
6. Phosphorus and Vertebrates.
    - (i) Occurrence and Distribution.
    - (ii) Growth requirements.
    - (iii) Distribution and Exchange.
    - (iv) Excretion.
    - (v) Metabolism.
        - (*a*) General.
        - (*b*) Use of radioactive phosphorus for diagnostic and therapeutic purposes.
7. Phosphorus and Proteins and Enzymes.

## PHOSPHORUS AND FOOD

Wide variations have been found to occur in the normal phosphorus content of foodstuffs.[1] The content of lean meat is greater than that of fat,[1a] while that of fish is twice that found in beef.[2] The mean phosphorus content of egg yolk (expressed as $P_2O_5$) is 1·42% but only 0·035% in the white.[3] The total phosphorus content of 53 French wheat samples varied between 0·80 and 1·41%, but 0·59–0·69% for Syrian wheat,[4] while that of Australian wheat was only 50% of that found in English wheat.[5] The phosphorus content of the flour prepared from these wheats was, however, only 20–25% of that of the whole grain.[4,6] Because of the great nutritional value of phosphorus, determinations have been made of the normal contents in typical foods occurring in the average diets of many countries, including Puerto Rico,[7] Belgium,[8] Brazil,[9] China[10] and the Philippines.[11]

The phosphorus content of human milk (0·22 g./l.) is much less than that of cow's milk (0·93 g./l.)[12] and the latter may range up to 2·73 g./l. or higher.[13] About 38% of the original phosphorus of milk is retained in cheese.[14–5] Only about 40% of milk phosphorus is dialysable[16] or removed by ion exchange resins[17] and the existence of several independent forms of phosphorus has been demonstrated by these means.[18] Techniques have been developed for separating the phosphatides of milk.[19] About 50% of the phosphorus of cereals is in the form of phytin[20–1] but the percentage of this form is increased in flour.[22] The phosphorus of potato flour is present largely in the form of polyose phosphates.[23] Many foods lose considerable amounts of phosphorus during preparation by steeping or cooking[24]; the phytin phosphorus of rice, for example, decreases from 0·435 to 0·116% on boiling.[25] Such losses tend to be greater for boiling than for steaming[26] but are not invariably high.[27] The loss of phosphorus on milling rice parallels the loss of thiamine.[28] There is a greater loss of phosphorus than of nitrogen during storage of orange juice.[29] Since spoilage of many foods is also accompanied by losses of phosphorus, determination of this element has been suggested as an index of quality,[30] though the ratio of phosphorus to calcium appears to be a better estimate of the suitability of peas for canning.[31] Exposure of foodstuffs to very intense radiation has not been found to induce radioactivity of the phosphorus contained in the food.[32] Vitamin *D* has been determined by bioassay following the parenteral use of $^{32}$P. The method has a wide range and is more sensitive than the normal assay.[33–4]

It has been shown that the improvement of human diet following the addition of milk and green foods is due largely to the additional calcium and phosphorus.[35] The feeding of milk labelled with $^{32}$P to dogs indicates that the milk proteins contain a bound form of phosphorus which contributes to the nutrition of young animals[36] and is assimilated more efficiently than calcium phosphate.[37] Cow's milk treated by base-exchange resins still contains adequate calcium and phosphorus for the nutrition of infants.[38] A higher phosphorus utilization by young children was obtained by feeding evaporated milk instead of pasteurized milk.[39] Inorganic phosphate has a curative effect on rickets and may lead to a false diagnosis in Vitamin *D* assays.[40] At the same time Vitamin *D* and calcium affect the availability to animals of the phosphorus of phytic acid.[41] Provided that the ratio of calcium to phosphorus in the diet is the same as that in which they are laid down in bone, Vitamin *D* does not appear to be essential for health.[42] Vitamin *D* may in fact depress the utilization of phosphorus in some cases.[43] The rate of calcification in young animals may be increased by raising the calcium and phosphorus contents of an already adequate diet.[44] There may be some advantage in varying the proportion of calcium to phosphorus in the diet as different body weights are reached.[45] Slightly better phosphorus assimilation occurs in rats in which the phosphorus source is $CaHPO_4,2H_2O$ than with $Ca_3(PO_4)_2$,[46] while the addition of $K_2HPO_4$ to the diet increases still further the growth of rats receiving calcium lactate, but not when administered alone.[47] More phosphorus is retained but less calcium is utilized by subjects on a diet of unpolished rice although the same amount of phytate phosphorus is available.[48]

The nutrition of cattle has received much attention because of its economic

**Refs. p. 1395**

importance. The phosphorus content of many cattle foodstuffs has been determined[49] and there have been several studies of the effects of cultivation on the content of pastures.[50-2] Calves require 10–16 g. of phosphorus per day up to 1 year.[53-4] Cows fed on alfalfa alone may receive inadequate supplies of phosphorus[55] and show signs of phosphorus deficiency.[56] This can readily be diagnosed by determinations of the blood serum phosphate content.[57] Phosphorus deficiency leads to a reduction in the milk yield of dairy cows.[58] An excess of phosphorus in the diet of cattle causes high serum phosphate values but no apparent adverse symptoms.[59] Serious cases of phosphorus deficiency are characterized by the chewing of wood and bones, the condition being readily cured by the addition of bone meal to the diet.[60] Calcium hydrogen phosphate,[61] sodium dihydrogen phosphate[62] and disodium hydrogen phosphate[62-3] appear to be utilized more efficiently by cattle than is bone meal. The availability to rats of the phosphorus of hay is less when the phosphorus content is low, possibly because of increased excretion in the faeces.[64-5]

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## PHOSPHORUS AND MICRO-ORGANISMS

The phosphorus content of many species of micro-organisms grown under standard conditions is fairly constant and reproducible and determination of the phosphorus content of a medium has frequently been used as a measure of the total number of organisms present in the medium.[1–3] Organisms grown in a medium containing radioactive phosphorus readily become labelled and determination of their specific activity is then a convenient means of estimating their number or dry weight.[3–5] Different species of micro-organisms may differ considerably in their normal phosphorus contents. Thus, among the yeasts, *Tortula utilis* has 36% more phosphorus than *Saccharomyces cerevisiæ*.[6] A virulent strain of the tuberculosis bacillus, *Mycobacterium phlei* had a normal phosphorus content three times as great as, and required a much more abundant supply of phosphorus in the medium than a non-virulent strain of the same species.[7]

Labelling of micro-organisms by the radioactive isotope, $^{32}$P, has proved of great value for tracing their fate during various transformations. Thus when labelled tubercle bacilli are injected into rabbits $^{32}$P is detected in the liver, lungs and kidneys.[8] Many fungicides have been shown to have a direct effect on the permeability of the fungal cell wall, permitting labelled phosphorus compounds to leak out.[9] The progeny of a single cell of *Micrococcus cryophilus* has been followed through eight generations and useful information obtained on the organization of the DNA of the cell.[10] Similarly labelled bacteriophage $T_2r+$ has been carried through two successive cycles of reproduction in bacteria and found to transfer 30% of the phosphorus at each cycle.[11] Bacteria and yeasts are very efficient in removing $^{32}$P but not iso-

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topes of the alkali metals from laundry waste water.[12] Higher specific activities are required to label bacteria for radioautography and satisfactory results are obtained with a content of $10^{-8}$ microcuries per cell, i.e., about 1000 phosphorus atoms per bacterium.[13] Although repeated passage of *Escherichia coli* through a medium containing $^{32}P$ had no apparent effect,[14] exposure of many species to an activity exceeding 5–10 μC./μg. of phosphorus causes growth inhibition.[13,15] The inhibitory and lethal effects of $^{32}P$ on many micro-organisms appears to be due to transmutation to $^{32}S$ rather than to the radiation.[13,16] It has been claimed that the inactivation of bacterial cells is due to those disintegrations which occur in the DNA[17] and a diminished capacity to transmit generic characters may be caused by $^{32}P$.[18] Addition of the isotope above a minimum of 0·02 μC. per culture to a *Staphylococcus* culture modified the pigmentation and virulence.[19] From the lethal effects of $^{32}P$ the diameter of the sensitive volume of *Escherichia coli* cells is estimated at 0·15 μ, which is larger than that estimated for *X*-rays (0·11 μ).[20]

Although labelled crown gall bacteria release much $^{32}P$ when transferred to a non-radioactive medium,[13] there is little exchange between cell and medium in the case of soil bacteria[21] and *Acetabularia*,[22] while the phosphorus of tobacco mosaic virus cannot be removed by dialysis.[23] The phosphorus taken up by *Escherichia coli* is rapidly incorporated into nucleoproteins and phospholipids.[24] *Micrococcus halodenitrificans* may later release a fraction of the labelled nucleoprotein as extracellular material when the external ionic atmosphere is changed.[25] Phosphorus is incorporated more rapidly into RNA than into DNA and there is no appreciable exchange of phosphorus between the two.[26] The phosphorus taken up by fowl cholera virus is partitioned in the ratio: 21% in the RNA and 65% in the phospholipids.[27] During the logarithmic growth phase of a culture, phosphate uptake is also logarithmic and both growth and uptake are independent of the external phosphate concentration down to $10^{-6}$ M. During the lag phase, however, organic phosphorus compounds are synthesized whilst the organic phosphorus content declines during the stationary phase.[28] The rate of turnover of all organic phosphorus compounds is increased by raising the supply of ammonia–nitrogen.[29] More than 97% of the phosphate taken up appears almost immediately in four simple sugar phosphates (adenosine triphosphate is the first compound to accumulate), and these then undergo further synthetic reactions.[30] The metabolism of many species of micro-organisms has been shown to involve oxidative phosphorylation, not only for the oxidation of simple metabolites[31–2] but also for the reduction of nitrate[33] and sulphate.[34] An enzyme has been isolated from *Escherichia coli* which causes polymerization of adenosine phosphate.[35] Antibiotics exhibit variable effects on phosphorus uptake and metabolism. Thus, penicillin causes the accumulation of phosphorus compounds in *Staphylococcus aureus*[36] but has no effect on the uptake of $^{32}P$ by *Micrococcus pyogenes*.[37] *p*-Aminosalicylic acid and *iso*nicotinoyl hydrazide increase the absorption of phosphorus by *Mycobacterium saprophyticum* and *M. smegmatis*[38] whereas streptomycin increases absorption by *M. avium*[39] and oxytetracycline has no effect on that of *Micrococcus pyogenes*.[40]

The permeability of the bacterial cell wall increases greatly on the death of the cell and the rate of loss of $^{32}P$ from cells to the medium approximates to the mortality rate.[41] The rates of loss were similar whether the bacteria were killed by heat, by phenol or by chlorination.[42] Cells of *M. pyogenes* are osmotically impermeable to phosphates and transport of this ion into the cell appears to be an enzyme-linked reaction.[43] Uptake of phosphate by *Amœba proteus* seems to be very dependent on the activity of the nucleus.[44] During the early stages of growth phosphate ions may accompany alkali cations into cells of *Basterium lactis aerogenes*.[45] The transport of labelled phosphate into *Escherichia coli* is largely via fructose phosphates to which the cell wall is highly permeable.[46] Azide ion markedly stimulates the uptake of phosphate by *Azotobacter vinelandii* at low concentrations but inhibits at higher concentrations.[47] The toxic silver ion increases the rate of loss of $^{32}P$ from fungal spores.[48] It has been found that orthophosphite does not interfere with enzyme reactions involving phosphate and can thus be used in buffers in many cases, but this

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finding does not hold for *A. vinelandii* the respiration of which is inhibited by orthophosphite.[49]

Infection of the cells of *Escherichia coli* by single virus of T1 or T2 bacteriophage causes a rapid loss of intracellular phosphate.[50] Polyhedral virus infecting silkworm larvæ behaves like a genuine parasite and appropriates the phosphate of the host cells.[51] The phosphate taken by T2 bacteriophage from the bacterial cell is, however, limited to that most recently absorbed by the bacterium from the medium, within two minutes of infection, and thus the host cell nucleoprotein is not utilized by the virus.[52] A fowl virus infecting *Amœba proteus* also took up only a very small fraction of the host phosphate.[53] Almost all the phosphate assimilated by the virus enters the nucleic acid fraction and there is no significant exchange of $^{32}$P between the combined and inorganic phosphate.[54] Studies using virus labelled with $^{32}$P show that 80% of the parent virus DNA is broken down to smaller fragments during reproduction.[55–6] There is some inactivation of bacteriophage by the disintegration of $^{32}$P and the rate of inactivation is reduced at low temperatures.[57–8] The lethal effect is again due not to the radiation but to the transmutation.[59]

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## PHOSPHORUS COMPOUNDS AND PLANT GROWTH

### Occurrence and Distribution of Phosphorus in Soils

Since phosphorus is an essential plant nutrient it is present in all soils which support plant growth. In unfertilized soils phosphorus largely arises from the decomposition of animal and vegetable matter, although rain has been shown to cause increases in soil phosphorus of the order of 0·55 kg./ha.[1] Phosphate ion applied as fertilizer is normally found in the upper 15–30 cm. of the soil, although the presence of vegetation can cause a gradual penetration into the deeper layers.[2–3] Thus, after 28 years of cropping with citrus the total phosphorus of a soil increased at all depths up to 36 inches,[4] but a grass cover caused the phosphorus to remain in the surface layers.[5] There is general agreement that the B horizons absorb and fix more phosphorus than either the A or C horizons[6–8] and the proportions of acid-, neutral- and alkali-soluble phosphorus differ in the three horizons.[9] Acid-soluble phosphorus in deep soil may first decrease to a minimum in the A horizon and then rise to a maximum in the C horizon.[10] Repeated annual fertilization has been found to increase the soil phosphorus content as much as fivefold,[11] this increase being confined to the upper few centimetres of the soil.[12] Mixing to greater depths may then be necessary to ensure the correct nutrition of deeper rooted trees.[13] The proportion of phosphorus in the organic form decreases with depth.[14–5]

The ratio of organic carbon to organic phosphorus varies so widely that there appears to be no relationship between the two, contrary to expectations.[16–8] In the surface layers about $33\frac{1}{3}\%$ of the total phosphorus is in the organic form, iron and aluminium phosphates accounting for another 50%, the remainder being absorbed. The corresponding figures for sub-soils are 20, 67 and 5% respectively.[19] In acid soils phosphorus tends to accumulate in alkali-soluble forms and in neutral or calcareous soils in acid-soluble forms.[20] About 45% of the organic phosphorus occurs in decomposable organic matter, the remainder being in the more resistant humus.[21] The

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effects of a number of physical factors on the synthesis of organic phosphorus have been studied in a variety of soils. The rate of synthesis is high initially but soon decreases. Alternate wetting and drying of the soil increases synthesis.[22] The organic phosphorus content of soil is increased by fertilization.[23] The reverse process of mineralization depends on the intensity of metabolism and is thus measured by the respiration of the soil.[24] By means of the radioactive isotope $^{32}P$ it has been shown that there may be a rapid turnover of phosphorus in certain phosphorus compounds and this lends support to the concept of a 'metabolic pool' of phosphorus from which bacteria and plants are supplied with assimilable phosphorus.[25] Recent work on the use of $^{32}P$ to study phosphorus transformations in the soil has been reviewed.[26] The seasonal variation of phosphorus in a cropped soil and a bare peat soil followed exactly opposite courses, the cropped soil restoring its reserves in winter and spring. This restoration was correlated with the metabolic activity of the soil.[27]

## Availability of Phosphorus in Soils

Many soils have the ability to convert phosphorus into a form not readily available to plants, the process being known as fixation.[28] Since the fixed phosphorus is soluble in acids only with difficulty, methods of determining the available phosphorus are often based on extraction of the soil with very dilute acids.[29] In some soils 70% of the added superphosphate fertilizer is fixed in the upper 4–6 inches.[30] It has been suggested that in acid soils at least the formation of iron and aluminium phosphates may be responsible for fixation[31–2] and this process almost certainly occurs in lateritic soils.[33] Although ferric oxide and alumina gels fix phosphate in an insoluble form, plants are able to utilize this phosphate during growth.[34] There is the possibility that in some cases the phosphate may be occluded in the iron oxide coatings of colloidal silicates.[35] There is a significant correlation between the amount of phosphate fixed and the soil colloid content.[36] Phosphate is fixed in the clay minerals by reaction with aluminium and iron originating from the exchange sites or from dissociation of the mineral.[37] In some cases a new solid phase has been observed to form on the surface of the mineral particles.[38] Calcium ions may stabilize the iron and aluminium phosphates[39] and fixation is in fact observed to increase with increasing calcium saturation.[40] In general, however, phosphate fixation is reduced as the degree of base saturation increases.[41] The predominant anion also appears to have an important influence on fixation.[42] Apparatus has been developed for determining the exchangeable phosphate in soil.[43] The percentage of phosphate firmly absorbed varies greatly with different soils.[44] The formation of separate phase crystals of phosphates by kaolinite and greenalite has been made the basis of a unified theory of phosphate fixation in soils.[45]

In some soils phosphate is rapidly leached[46] and carried into deeper strata.[47] Such leaching losses may be very important in mountainous districts.[48] There is little evidence for lateral movement of phosphate.[49] Leaching is fairly rapid in light sandy soils,[50] but normally the phosphate is fixed in the upper horizons unless the soil is degraded by water-logging, etc.[51] Phosphate added as the ammonium, sodium or potassium salt moves downwards much more rapidly than that applied as superphosphate,[52] as might be expected from solubility considerations. Simultaneous addition of ammonium sulphite or sodium nitrite accelerates the penetration of rock phosphate.[53] Phosphate is more mobile at lower pH values.[54] Trials show that there is little danger of serious loss of phosphate through leaching following autumn application.[55]

Recent work on the availability to plants of soil and fertilizer phosphate has been reviewed.[56] Organic phosphate appears to be largely unavailable to plants and must be first mineralized by bacterial action.[23, 57] Superphosphate and ammonium phosphate are equally available.[58–9] Addition of sulphur to soil containing rock phosphate increases both the growth and the phosphorus content of oats and clover.[60] Where fixation takes place considerable additions of fertilizers may be required to increase the phosphorus content of crops and the increase may not occur in the edible portion.[61] A multiple regression equation has been derived for non-calcareous soils indicating the relationship between available phosphorus, inorganic phosphate and organic phosphate.[22] An excess of available phosphorus may cause symptoms of toxicity in some crops and the amount of superphosphate required to produce such symptoms varies between 5 tons/acre in clay soils and 4 cwt./acre in sands.[62] Similarly the growth of apple trees has been found to be adversely affected by fertilization with apatite, iron or aluminium phosphates but not by magnesium pyrophosphate.[63] Cultivation of a brown forest soil tends to increase the organic phosphate and to decrease the soluble portion.[64] Amounts of phosphate taken up by grasses are related to the degree of saturation of the base exchange of the soil.[65] Nitrogen fertilization was found to increase the phosphorus availability of soils,[66] possibly through an effect on the pH value.[67] There appears to be an optimum ratio of nitrogen to phosphorus for maximum uptake by crops.[68] Sterilization of soils by ethylene oxide increases the available phosphorus.[69] Although oats could not utilize the phosphorus of undecomposed phytin,[70] the intact roots of some crop plants are able to absorb this form of phosphorus (without mineralization) owing to the presence of the enzyme phosphatase in the root cap.[71] In general plant residues decompose and give up their phosphorus gradually over a period of some months.[72] Carbon dioxide may be an active agent in causing the release of available phosphorus from minerals.[73] The solubility of soil phosphorus is decreased by storage of the soil in either a dry[74] or a moist state[75] but is considerably increased by alternate moistening and drying. There are conflicting reports of the action of calcium on the availability of phosphorus[76]; in some cases liming increased the amount of phosphate absorbed by plants,[77] in other cases the opposite resulted.[78] The action is probably complex but part of the effect is a result of pH changes.[79] Thus the water-soluble phosphate decreased from 20 to 4 mg./100 g. of soil as the pH was increased from 4·3 to 6·7 by liming.[80] Significantly the various calcium phosphates are stable in the following pH ranges: monobasic pH 3·0–5·0, dibasic pH 5·0–6·4 and tribasic above pH 6·4.[81]

### DETERMINATION OF AVAILABLE PHOSPHORUS

A great deal of attention has been focused on the problem of determining the amount of phosphorus in soils actually available to plants. The most direct method is a biological one in which plants are grown in the soil under closely defined conditions and the phosphorus content of the plant is determined at harvest. Analysis of a crop plant by Mitscherlich's method[82] is occasionally used but is regarded in general as too time-consuming. More rapid methods have thus been evolved including the use of bacteria[83] and fungi such as *Aspergillus niger*,[84,86] or *Cunninghamella sp.*,[85] but the most widely used of these methods is that of Neubauer in which test seedlings are grown under controlled conditions.[87-9] Tests using fungi often give conflicting results.[90-1] The time and labour required for these biological tests have stimulated interest in the development of a rapid chemical method for determining available phosphorus. The phosphorus present in soils may be classified as difficultly-soluble, acid-soluble and water-soluble; only the last is readily available to plants. Acid-soluble phosphorus is available to a limited degree but may first require conversion into an easily-soluble form.[92] The difficulty in the determination is thus that of devising a method of extraction which removes the available phosphorus only; determination of the phosphorus in this extract is done by a colorimetric method such as a modification of the Denigès or Fiske–Subberow method.[93-5] Extraction methods include the use of 0·002 N. sulphuric acid (Truog),[96] 0·03 N. ammonium fluoride plus 0·025 N. or 0·1 N. hydrochloric acid (Bray),[97] 1% acetic or critic acid (Dyer),[98] sodium bicarbonate,[99] lactic acid (Egner)[100] or a mixture of sulphuric and acetic acids.[101] Careful comparison of the chemical with the biological methods indicates that no one chemical method is satisfactory for all soils.[102] The Truog method appears to be the most useful for soils of low fixing capacity and the Bray method for those of high capacity.[103] A study of the solubility of phosphates in sulphuric acid solution indicates the value of solutions as strong as 0·2 N.,[104-5] but the

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standard Truog method may dissolve more phosphorus than is available to plants.[106] The Bray method using ammonium fluoride plus hydrochloric acid gives results agreeing with the sodium bicarbonate method and with the crop yield on calcareous soils[107-8] but gives high results with volcanic soils containing much alumina.[109] Other workers have obtained good results with the Egner method[110] but the acetic acid[111] and citric acid[110,112] methods appear unsatisfactory. The correlation between crop yield and chemical method varies with the crop,[113] but determination of the total soil phosphorus is superior to any extraction method.[114] Good correlation has been obtained between crop response and the amount of phosphorus removed from the soil by electrodialysis.[115] Among the biological methods, the *Aspergillus niger* method agrees with most chemical methods.[116] The Neubauer method tends to give slightly lower values of available phosphorus than the Truog method.[117] The Mitscherlich method did not agree with the Egner or Neubauer methods.[118] The influence of soil pH on the absorption of phosphorus in the Neubauer test has been investigated.[119] This test indicates that a soil is deficient in phosphorus at levels of 8 mg./100 g., or less in 75% of cases examined, the corresponding Egner values being about double this content.[120] Foliar analysis gives excellent correlations with soil analysis of some soils but not all.[121-2] Analysis of sugar beet petioles appears to be a very efficient method of determining the available phosphate of a soil.[123] Evaluation of available phosphorus by comparing the slopes of biological responses may not always be valid.[124] Although in general organic phosphorus does not contribute to the available phosphorus, this may not be true at high soil temperatures when the rate of mineralization of such phosphorus is greatly increased.[125-7] Determination of soil organic phosphorus is usually based on determination of the phosphorus liberated by oxidation with hydrogen peroxide.[128-9]

### THE PHOSPHORUS CYCLE IN SOIL

There is a well-defined cycle of phosphorus in soil and the citrate-soluble phosphorus content of soil is directly related to the bacterial and mould populations.[130] The phosphorus and nitrogen cycles appear to be interdependent[131-2] and phosphorus not only stimulates the assimilation of nitrate–nitrogen but also prevents its leaching.[133] Phosphorus also stimulates the nitrogen-fixing capacity of *Azotobacter*.[134] A group of organisms classed as *Nucleobacter* are able to split off inorganic phosphate from nucleoproteins in soil,[135] while *Bacillus megatherium* var. *phosphaticum* actively produces soluble phosphorus compounds.[136] Many moulds assimilate soluble phosphorus and one has been found to solubilize insoluble phosphorus.[137-8]

### EFFECTS OF PHOSPHATE FERTILIZERS

The use of the radioactive isotope $^{32}P$ has thrown new light on many of the problems of the uptake of phosphorus from fertilizers and their use has recently been reviewed.[139-40] All rates of application of phosphate fertilizers increase crop yield except when manure is used[141] and the uptake by the plants is correlated with the decrease of available phosphorus.[142] Careful application of the Mitscherlich equation enables differentiation to be made between the phosphorus taken up from the soil and from applied fertilizer.[143] The phosphorus of superphosphate is much more available to plants than that of rock phosphate[144] and the uptake from the former is independent of pH whereas the uptake from the latter fertilizer is inversely related to the pH.[145] Assimilation of phosphorus from a series of phosphates was greatest from magnesium hydrogen phosphate[146] but in other trials ammonium phosphate was best.[147] The most efficient fertilization is achieved when a source of readily available phosphorus is applied in the early stages of growth[148-9] and uptake by young plants has been observed within 1 hr. of application. As might be expected, uptake depends to a great degree on the distribution of fertilizer in the vicinity of the seed,[151] although all phosphate ions in the soil have the same probability of being absorbed.[152] All the inorganic phosphate ions in soil undergo exchange with

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added phosphates[153] and prolonged fertilization is found to increase greatly the amount of exchangeable phosphorus in the soil.[154] There is often rapid disappearance of added phosphorus which may be partly taken up by bacteria[155] and absorption of phosphorus by plants from superphosphate proceeds more rapidly when the phosphate is no longer in an easily water-soluble form.[156] There is also a good correlation between the precipitation and movement of phosphorus in the soil.[157] The uptake of phosphorus by plants is more rapid from granular fertilizers than from powders.[158]

Studies of the diffusion of phosphate ions in soil suggest that the passage of phosphate from soil to solution is more complex than a simple solution of a definite chemical form[159] and is dependent on the water:soil ratio.[160] Only a small fraction of the total phosphorus is easily diffusible.[161] The distribution of ions at the soil–water boundary may represent a Donnan equilibrium.[162] The diffusion of phosphate ions from soil particles has been demonstrated in agar gels containing molybdate reagent and shown to be dependent on the particular-size distribution in a sandy soil.[163] Kinetic exchange studies in soils show the presence of two points of inflection which are not due to either ferric or aluminium phosphate.[164–5] Phosphate ions may be very firmly absorbed by some soils,[166] the isotherms being of the Langmuir type.[167] Although absorption is greater in acid than in alkaline soils this is probably of little importance for the fixation of phosphorus.[168]

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## Phosphorus as a Fertilizer

In some cases phosphate fertilizers have been shown to be very long-acting, crop responses being obtained 50 years after application.[1] The actual concentration of phosphate ion in the soil water required for plant growth may be as low as 0·05–2 p.p.m.[2–3] The optimum nutrition of crop plants depends in general on a balanced fertilization of nitrogen, phosphorus and potassium, the so-called N–P–K ratio. A decrease in the optimum supply of any one of these may lead to increased or decreased absorption of the other two depending on the particular crop.[4–5] The effect of nitrogen and potassium on phosphorus uptake appears to vary at different stages in the growth of rice,[6] while only in the early growth stages of wheat did phosphorus fertilization affect the phosphorus content of the crop; otherwise the nitrogen supply alone controlled the phosphorus content.[7] The relationship between nitrogen and phosphorus fertilization is complex. Thus an increase in nitrogen supply did not affect the phosphorus uptake by coffee, whereas application of phosphorus fertilizer

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decreased the nitrogen content of sugar cane or sorghum.[8] Nitrogen fertilization may double the rate of uptake of phosphorus by wheat and oats when the phosphorus supply is low.[9] A reciprocal relationship appears to exist between phosphorus and nitrogen in oranges, and a high nitrogen supply is essential for the synthesis of organic phosphate.[10] Ammonium salts increase utilization of phosphorus more than do nitrates,[11-2] and conversely an adequate supply of phosphate is necessary for the utilization of nitrate.[13] Orange trees take up more phosphorus when treated with organic nitrogenous manures than with quick-acting fertilizers such as ammonium sulphate.[14] Basic phosphate and calcium hydrogen phosphate tend to favour the uptake of nitrogen by grape vines, while superphosphate favours uptake of potassium.[15] An increase of phosphorus fertilization decreases the calcium content of the chlorophyll of sugar-cane leaves but increases the magnesium content.[16] Conversely, phosphorus utilization by barley is increased by the addition of magnesium.[17] Little work has been done on the effect of anions on phosphorus utilization. Chloride increases the phosphorus uptake of potatoes,[18] while addition of elemental sulphur to neutral or alkaline soils increases the availability of phosphorus from less efficient fertilizers such as dicalcium phosphate.[19] Silicate tends to enhance the uptake of phosphorus by wheat,[20-1] while nickel ions reduce the uptake of phosphate by tomatoes.[22]

Green manuring is an efficient means of supplying phosphate[23] and a relatively greater amount of phosphorus is utilized by plants from compost than from non-composted plant material.[24] Green manures supply more of the available forms of phosphorus than do mineral fertilizers.[25] During composting much of the phosphorus may be fixed in bacterial cells and be subsequently liberated on the death of the micro-organisms.[26]

### FOLIAR ANALYSIS

The necessity for a rapid chemical test of the nutritional status of a particular soil for a specific crop has led to the development of foliar analysis in which selected leaf samples are ashed and assayed for total phosphorus content.[27-8] The definite establishment of a simple minimum phosphorus content is usually impossible since the requirement closely depends on the nitrogen content of the leaves,[29-30] and some workers have attempted to lay down minimum[28] or optimum[31] leaf compositions in terms of a complete analysis of potassium, nitrogen, phosphorus, etc. The uptake of phosphorus by apple trees is strongly dependent on the magnesium and potassium contents of the leaves.[32] Variation in phosphorus contents is found among leaves taken at different levels along the stalk[33] and at different positions on the tree.[34] The percentage of phosphorus decreases with the age of the leaf owing to translocation into the younger developing regions.[35-8] There may, however, be some relationship between leaf phosphorus content and availability of phosphorus in the soil during the early part of the growing season.[39] No general relationship could be deduced between the phosphorus content of barley and the type of fertilizer used.[40] In spite of the lack of correlation between total soil phosphorus and leaf phosphorus content, the latter is closely related to fruit quality.[41] There is a close relationship between the amount of phosphorus found in the leaves of red oak, chestnut and red maple and the amount of phosphorus applied as fertilizer,[42] but the actual amount found in the leaves varies widely with the genus but not with the species.[43]

### FOLIAR FEEDING

It has been found that phosphate ion can be absorbed through the leaves of plants and this has led to the development of 'foliar feeding'. Studies with the radioactive isotope $^{32}P$ show that in some species of plant considerable quantities of phosphorus are absorbed through the leaves and translocated to the roots,[44] though there is also a tendency for the ion to accumulate in the rapidly growing aerial parts.[45-6] The

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younger leaves absorb phosphate much more readily and both absorption and translocation tend to decrease with the age of the plant.[48] The rate of entry into apple trees is greatly increased through damaged bark.[49] Upper leaf surfaces had a greater rate of absorption than lower surfaces in spite of the smaller number of stomata.[50] Absorption is enhanced by light[50] and temperature.[50-1] Soya-bean leaves absorb 15% of the phosphate applied to the leaves within the first two hours,[52] and a large percentage of that absorbed is rapidly taken into the metabolic cycle as sugar phosphates.[50, 52] Three-year trials suggest that the technique of foliar feeding may be most effective when applied at the time of flowering.[53] Phosphorus is utilized 20 times more efficiently by foliar feeding than by soil application.[54] A considerable percentage of the absorbed phosphate content has been observed to pass out of the plant again through the roots.[55] When sprayed in admixture with $^{32}PO_4'''$, insecticides have no effect on the rate of absorption but calcium salts are definitely inhibitive.[56] Foliarly applied phosphate tends to reduce the leaf contents of nitrate,[57] calcium[58] and magnesium.[58]

## Deficiency of Phosphorus in Plants

A restricted supply of phosphorus below 0·2 p.p.m. in culture solutions leads to deficiency symptoms in citrus[59] while the growth of *Chlorella pyreoidnosa* ceases below a content of $10^{-7}$ μg. of phosphate per cell.[60] The unicellular marine plant *Nitzschia closterium* after growth in light under phosphorus-deficient conditions incurs a 'phosphorus debt' which is repaid by increased absorption of phosphorus in the dark.[61] Among higher plants such as maize, deficiency symptoms do not often appear during slow growth with restricted total nutrient supply, but only when the balance of nutrients is upset by additional supplies of nitrogen.[62] Phosphorus deficiency symptoms appear in citrus when the phosphorus content of the leaves is below 0·05%.[63] The first symptom in orange trees appears as a loss of quality in the fruit and only when deficiency is more acute are the foliage and growth affected.[64-5] Phosphorus deficiency symptoms have been described in many crop plants.[66] In tobacco deficiency of phosphorus leads to an abnormally dark green immature plant which fails to ripen satisfactorily[67-9]; in sugar cane retarded growth, absence of tillering, abnormally large root systems and narrow leaves[70]; in rice restricted root growth[71]; in potatoes a reduction in crop.[72] Phosphorus deficiency in other plants is associated with unusual pigmentation such as a red-purple discoloration of pine needles[73] and in many instances coloured spots appear resembling those caused by disease.[74-5] In some cases phosphorus deficiency may render a plant more susceptible to attack by a fungus such as the *Pythium* root rot in cereals.[76] The *Myitpo* disease of rice paddy in Burma is not strictly a deficiency disease since the roots contain an abnormal amount of phosphorus which the plant is unable to utilize.[77] Excessive supplies of phosphorus may prove toxic to plants, by producing copper deficiency in citrus for example,[78] or by producing physiological disturbances in cereals.[79-80]

## Uptake of Phosphorus by Plants

Studies with nutrient solution suggest that the absolute concentration of phosphate in the solution is the most important single factor controlling the uptake of the ion by the plant.[81] There is, however, evidence that in some soils direct root–soil contact is necessary.[82] The number and character of the secondary roots are certainly important factors and the rate of uptake is not related simply to the concentration of the ion in the soil solution.[83] Attempts have been made by using the Mitscherlich equation to calculate the contribution to plant nutrition of three forms of phosphate: the direct fertilizer, the absorbed phase and the soluble phase. It is concluded in the case of wheat that the absorbed phase is more important than the soluble form.[84] Phosphate ions may be adsorbed on to ion-exchange resins without loss of biological activity.[85] The amount of phosphorus absorbed depends on the amount already present inside the plant tissues.[86] Attention has been directed to the variations in uptake of phosphorus in different regions of the same plant.[87] The rate of assimilation of phosphorus varies with the age of the plant. Thus rye sprouts exhibit a minimum rate at 5·3 days after sowing and the greater part of the phosphorus is taken up in 6–15 days.[88] The rate of uptake by *Andropogon ischæmum* undergoes two maxima within the first six weeks of growth,[89] but in sugar cane[90] and pineapple[91] the rate of uptake is essentially constant during the first year. The uptake of phosphorus is greater through shallow lateral roots than through the deeper root system,[92–3] and the absorbed phosphorus tends to accumulate in the lateral roots prior to movement into the plant stem.[94]

Uptake by non-mycorrhizal plants tends to occur in two phases, first as initial rapid uptake, the rate of which is inversely related to the phosphorus content of the plant, followed by a second slower, uptake, whereas mycorrhizal plants have a more constant and higher rate which is independent of phosphorus content.[95] It seems to be well established that mycorrhizal growth results in increased uptake of phosphorus by many species,[96–8] but this does not appear to be due to greater utilization of organic forms of phosphorus.[99] The rhizosphere bacteria may play a part in the absorption of phosphorus by converting the element into a form more readily absorbed by the plant.[100] The rate of uptake of phosphorus increases with the rate of transpiration.[101] A small percentage, about 1%, of the absorbed phosphorus may be excreted by the roots.[102] The effect of temperature on phosphorus uptake appears to depend to a great degree on the plant. Thus absorption by millet is little affected by temperatures up to 40° whereas with winter wheat the rate of absorption is highest over the range 1–10°.[103] Uptake of phosphorus by cereals increases with the amount of applied irrigation water,[104] although roots preconditioned at low moisture conditions absorb more phosphorus than those conditioned at higher water levels.[105] Similarly roots absorbed most phosphorus from solutions of the same pH as that to which they had been conditioned.[106] The influence of pH on uptake is more marked in dilute than in concentrated nutrient solutions.[107] The presence of iron in solution resulted in a minimum rate of absorption at pH 5·0 owing to the lowered solubility of ferric phosphate at this pH.[108] Absorption of phosphate by many plants is reduced at low oxygen concentrations in the soil, but this effect may depend largely on the translocation from the roots.[109] In general uptake is little affected until the oxygen concentration falls below 10%, but uptake is stimulated by 5% of carbon dioxide.[110] Uptake of phosphorus by rice is strongly inhibited by hydrogen sulphide in the soil.[111] Addition of silicic acid to the soil increases the absorption of phosphorus by plants.[112] Aluminium oxide and humic acids behave similarly.[113]

The radioactive isotope $^{32}P$ has proved very useful for the study of plant nutrition.[114] The isotope must of course be used at such a level that radiation damage to the plant is minimized.[115–6] Movement of the isotope through the plant may be followed by autoradiography[117] or with the aid of a Geiger counter.[118] When superphosphate is applied to sugar cane 80–90% of the leaf phosphorus comes from the fertilizer.[119] Phosphorus is taken up more readily from calcium dihydrogen phosphate and from magnesium hydrogen phosphate than from tricalcium phosphate[120] and is absorbed as the orthophosphate ion,[121] although organic phosphates are readily assimilated.[122] The absorbed phosphate is very rapidly converted into organic phosphate.[123] Over 90% of the phosphate present in a solution was taken up by wheat grain and seedlings in 13 days[124] and equilibrium between absorption and translocation occurred after about 20 days.[125] The percentage of initial phosphorus absorbed plotted against concentration shows a well-defined maximum.[126] Phosphate absorbed by *Nitella* appears to be located almost entirely in the protoplasm.[127] The mycorrhizal fungus *Cortinarius glaucopus* after exposure to $^{32}P$ and subsequent inoculation onto the roots of pine seedlings is able to transfer this isotope to these seedlings.[128] Phosphate may be absorbed through the stems and branches of many woody plants,[129] but as might be expected damaged leaves absorb more rapidly than intact ones.[130]

## TRANSPORT OF PHOSPHORUS IN PLANTS

Phosphorus is translocated in plants at rates of 1·2–1·4 m./hr. in roots,[131] 64 cm./hr. in stems[132] and 2·4 cm./hr. in leaves.[125] There appears to be a slow continuous interchange of phosphorus between different leaves.[133] Phosphorus is largely taken up into the various parts of the plant during active growth and subsequent exchanges are slow.[134] The phosphorus of seed is transferred to the developing plant even in the dark.[135] The highest and thus usually the youngest leaves take up most phosphorus.[136] The content of phosphorus decreases from the base to the tip of the leaves.[137] Translocation in winter is very sluggish in many woody plants such as the white oak or alder, but not in conifers such as pines or red cedar.[138] In spring almost half of the phosphorus of stems and roots of woody plants migrates to the leaves[139] and flower buds.[140] The phosphorus content of the leaves of deciduous species continues to increase so long as they remain green, but in autumn as the leaves yellow a large percentage of the phosphorus is returned to the stem and shoots.[141] The total loss of phosphorus in fallen leaves at leaf fall varies between 35 and 90% of that originally present depending on the species.[142] A similar movement occurs in grain.[143] Movement of the phosphorus inside the plant may depend on concentration gradients resulting from the interconversion between soluble and insoluble forms.[144] In self-rooted plants phosphorus absorbed by one root is translocated to one group of branches only, whereas in grafted plants each root feeds all the branches.[145-6] Although there is little lateral movement of phosphorus in the conducting vessels of cacao trees,[147] many conifers and foliate trees exhibit free horizontal movement in the trunk.[148] Translocation is slow in the bark but rapid in the xylem and there is rapid lateral transfer between bark and wood when these are in contact.[149] The isotope $^{32}P$ appears in the xylem only after considerable accumulation in the roots and the main upward movement is due to transpiration.[150] Injury to the sap wood does not prevent upward translocation.[151] Very little phosphate penetrates the bark unless this is injured.[152-3] More phosphate is carried by the outer layer of the stem of *Pelargonium* than by the vascular system.[154] The greatest transport is through the phlœm of willow where $^{32}PO'''$ and $^{14}CO_2$ move in opposite directions.[155] The accumulation of phosphorus in leaves depends on illumination and is clearly dependent on carbohydrate metabolism.[156-7] Uptake and transport of phosphate increase with transpiration[158] and the transpiration rate of rape is higher for phosphorus-deficient plants.[159] Uptake of $^{32}P$ is reduced during the wilting of tomato plants and phosphate is transferred from leaves to stem.[160] Translocation of phosphate is dependent on the concentration in the plant of calcium,[161] boron[162] and iron[163] and is reduced by certain herbicides, fungicides and insecticides[164-5] and by soil fumigation.[166] After foliar application, $^{32}PO_4'''$ is translocated out through the roots into the soil and may be taken up by neighbouring plants.[167-9] There is also some loss from leaves by direct leaching.[170-1]

## DISTRIBUTION OF PHOSPHORUS

The normal phosphorus contents of different plants grown on the same soil vary widely with the species, from 0·163% for celery to 0·952% for tomato.[172] In general weeds are found to be richer in phosphorus than wild grasses,[173] while legumes are still richer.[174] The phosphorus content of castor bean hulls varied little with varieties but varied widely with years and locations,[175] whereas there was considerable variation among hybrids of sugar beet and mangel-wurzels.[176] The distribution of $^{32}PO_4'''$ in various tissues and organs has been followed by autoradiographic[177] and Geiger counting techniques.[178] The content of wheat varies widely from 0·328% in flour to 1·485% in the bran.[179] The distribution in grain crops depends on the point in the growth cycle at which the phosphate is added. Thus if added at the earing stage, phosphorus accumulates in the roots and is never translocated to the ears.[180] The total phosphorus content of germinating acorns and soya-beans remains constant, the phosphorus being transferred from cotyledons to embryo.[181] The distribution in tomato plants is affected by the growth promoters heteroauxin and 1-naphthylacetic acid.[182] During growth complex changes take place in the forms in which phosphorus occurs in the growing plant[183] and in the leaves during autumn yellowing.[184] Techniques have been developed for determining the various organic forms of phosphorus by means of radioactive phosphorus.[185] Approximately 75% of the phosphorus is in a soluble form in winter wheat up to the time of heading; this form then decreases to 50% or less.[186] In wheat bran 86% of the total phosphorus is in the phytin and only 17% occurs as phospholipid, whereas the germ contains 48% as phytin and the endosperm has very little phytin.[187] The structure of the phosphohexoses and phosphotetroses produced from potato starch by $\alpha$-amylase degradation has been determined by end-group analysis.[188] The major phosphate ester of plant sap has been identified as phosphorylcholine. Its zwitterion structure and solubility properties suggest its importance as a carrier for the penetration of phosphate through plant membranes.[189] $\alpha\alpha'$-diglycerophosphate is present in high concentration in *Scenedesmus*.[190] Inhibition studies indicate that the enzyme system responsible for the uptake of phosphate by loblolly pine roots has azide- and fluoride-sensitive components[191] and that mycorrhizal roots differ physiologically from non-mycorrhizal.[192] Cyanide ion is an inhibitor of phosphorus uptake by potato tuber slices.[193]

### Metabolism of Phosphorus

During the ripening of seed, phosphorus is continuously transformed to phytin, nucleic acid and lipid forms which slowly break down on storage of the seed with liberation of inorganic phosphorus.[194] Light has no effect on the pattern of distribution of phosphorus compounds in wheat during vernalization but does have an effect during later growth.[195] Oxidative phosphorylation has been shown to occur in homogenates of seedlings of *Phaseolus*.[196] A light-sensitive phosphorylation occurs in chlorophyll-free cells of barley and in yeast cells.[197] Intact chloroplasts transform light energy into adenosine triphosphate (ATP) by a photosynthetic phosphorylation which does not require oxygen[198] although phosphorylation is higher in aerobic conditions.[199] A positive correlation has been demonstrated between photosynthetic activity and the phosphorus content of cells.[200–1] Radioactive phosphorus has proved a useful technical aid for the study of the intermediate reactions of photosynthesis and detailed techniques have been developed for isolation of the intermediate products.[202–3] The initial conversion of soluble phosphate into an insoluble form is very rapid and carbon dioxide is necessary.[204] The concentration of phosphorylated metabolites changes when plants are transferred from light to darkness.[205] Phosphorus is also required for the photoreduction of carbon dioxide.[206]

In tomatoes on a deficient phosphorus supply, nitrate reductase activity decreases and nitrate thus accumulates.[207] An inadequate phosphorus supply affects the reproductive more than the vegetative tissues of cotton[208] and also appears to limit protein synthesis in wheat.[209] The chromosome volume in root tips supplied with an excess of phosphorus is usually nearly twice that of roots deprived of phosphorus.[210] Obligate parasites such as rusts and mildew cause an accumulation of $^{32}PO_4'''$ at the site of infection.[211]

The growth of pollen tubes may be followed by labelling the pollen with $^{32}PO_4'''$.[212] Autoradiography shows that phosphorus is directly incorporated into nucleic acids during formation[213] but the shoot cannot synthesize sufficient nucleic acid for its requirements and migration of nucleic acid from the root makes good the deficit.[214] Labelled phosphorus is taken up and incorporated into the nucleic acids of tobacco mosaic virus infected tomato leaves, but the virus does not affect the normal phosphorus metabolism processes of the leaves.[215] In crown gall tumours, owing to infection of *Pelargonium* by *Agrobacterium tumefaciens*, $^{32}P$ accumulates markedly.[216] The herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) greatly reduces the upward movement of phosphate to the leaves,[217–9] and causes an increase in total phosphorus in the stem.[220] This herbicide and its analogues cause blockage of metabolic processes so that the total phosphate content of the leaves declines, although the ratio of organic to inorganic phosphorus in the leaves may increase.[221–3] Radioactive phosphorus has been used to study the uptake, translocation and metabolism in plants of systemic organophosphorus insecticides such as Systox,[224] Schradan[225–6] and many experimental compounds.[227] Insecticides of this type do not appear to affect the biochemical reactions of plants to the same degree as 2,4-D.[228]

Care must be taken when working with the radioactive isotope $^{32}$P lest radiation injury be caused to the plants sufficiently to obscure or vitiate the experimental results. Although radiation injury to barley is apparent at a specific activity in the plant tissue[229] of 5·6 mC./g. of $^{32}$P, the effects produced by doses as high as 30 mC. of $^{32}$P per gram of inactive $^{31}$P are slight and not objectionable in nutrition experiments.[230] The damage is caused mainly by radiation dosage due to phosphorus inside the cells and not that in solution outside the tissues.[229] The most consistent symptoms of low doses are an increase in the absorbed phosphorus translocated to the roots and a reduction of root weight due primarily to an interference with metabolic processes.[231] Low doses of *X*-rays cause a rapid decrease in the amount of phosphorus taken up and a reduction in synthesis of nucleic acids.[232] Cell division may cease due to direct action on meristems at higher doses, the shoot being more sensitive than the root tips.[223] Very low doses of $^{32}$P cause a slight decrease in the number of mitoses, but as the dose increases there is a sharp decline.[234] Doses of $^{32}PO_4'''$ of 2·7–10·8 μC. per seed for 3–9 days produced mutants in tomato seeds.[235]

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## PHOSPHORUS AND AQUATIC ORGANISMS

Most natural waters have a low phosphorus content[1] except streams draining through phosphate mineral areas.[2] The abundance of many marine organisms, notably plankton and diatoms, has been shown to be directly dependent on the phosphate content of the water.[3] The normal ratio of nitrate to phosphate in the sea is about 9:1 by weight.[4] By means of the radioactive isotope $^{32}P$ it has been shown that ionic exchange between lake mud and water is an important cause of the observed seasonal variation in phosphate content.[5] Much of the variation may also be attributed to the activity of micro-organisms, notably bacteria.[6] The concentration of phosphate in estuarine waters was found to reach a maximum in August and to

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decline sharply in early September. There was also a decrease during the hours of darkness.[7] Variations of phosphorus content in the sea cannot be correlated with changes in salinity.[8] Inorganic phosphate is converted to organic forms by photosynthesis in phytoplankton in the upper layers of water. The plankton then sinks before decomposing to release the phosphorus.[9] Analysis of plankton in the Western Atlantic showed a phosphate content of 1·35% with a carbon to phosphorus ratio of 1:0·0273. The annual dissolved phosphate requirement for photosynthesis is estimated to be $75{\cdot}6 \times 10^{-5}$ g./sq. cm. of surface.[10] Most of the phosphorus associated with plankton is liberated within 24 hr. of its death.[11] Inorganic phosphate undergoes a cycle of bacterial assimilation and regeneration in the sea in which the phosphate is removed from solution for short periods.[12] In lakes and freshwater reservoirs the great bulk of the total phosphorus is in the form of insoluble compounds in the bottom sediments and this fraction is rendered soluble by the action of bacteria.[13] The limiting factor controlling the growth of plankton is the amount of assimilable phosphorus available[14] and the population peaks occurring throughout the year are closely correlated with available phosphorus.[15] The ratio of dissolved nitrogen to phosphorus is also important, the optimum ratio being about 10 parts of nitrate nitrogen to 1 part of phosphate phosphorus, although phytoplankton prefers ammonia as a nitrogen source.[16] There have been many attempts to use artificial fertilizers in fish ponds and lakes[17] and, although marine algæ respond to addition phosphate at 0·02 g./l. of $Na_2HPO_4,12H_2O$,[18] concentrations 4 times as large do not stimulate the growth of phytoplankton and still higher concentrations suppress growth.[19] It has been suggested that algæ growing in a lake with less than 1 μg./l. of phosphate obtain their supplies directly from suspended colloidal clay rather than through the intermediary of soluble phosphate.[20] The possibility of controlling the growth of algæ in freshwater lakes by reducing the concentration of nitrate and phosphate has been discussed.[21]

Determinations have been made of the phosphorus content of 322 species of marine invertebrates,[22] 20 species of fish[23–4] and many species of marine algæ.[25–6] The phosphorus content of the blood of fish is usually very high, approximately 3–4 times that of beef blood,[27] but the electric eel has a particularly low blood phosphorus content.[28] Analyses made for calcium and phosphorus in trout at all stages of life show that initially phosphorus is predominant but calcium soon reaches equivalent proportions.[29] The calcium–phosphorus ratio varies widely in different species from 0·42–0·73 in herrings to 1·57–0·65 in *Scomber scombrus*.[30–1] The phosphorus content of different organs and muscles has been determined for the pearl oyster[32] and for *Balanus physalus*.[33] Unusually high contents occur in minnow eggs[34] and in the starfish.[35] The blood-phosphorus of the crab *Maia squinado* rises to a maximum during the moult but falls again thereafter.[36] The phosphate content of a number of species of mollusc shells fluctuates considerably at different times of the year and in different localities.[37] Molluscs take up the isotope $^{32}P$ and its distribution in different tissues has been studied with a view to elucidating the mechanism of shell formation.[38–40] Similarities are noted between shell formation and calcification of mammalian teeth.[41] Labelled phosphate in solution is rapidly taken up by carp and distributed throughout the organs and tissues.[42] The freshwater mollusc *Helisoma duryi* concentrates the absorbed phosphate largely in the liver and pancreas.[43] The uptake of phosphate ions by crustacea may be under hormonal control, for removal of the eyestalks in *Hemigrapsus nudus* markedly affects uptake, the direction of the change depending on the stage of the moult cycle.[44] Pretreatment of *Xenopus blastulæ* with solutions of lithium and sodium salts increased subsequent uptake of $^{32}P$ very greatly.[45–6] Uptake of $^{32}P$ by the sea urchin *Strongylocentrotus purpuratus* is greatly increased during cleavage and blastulation but decreases in later stages.[47] The cephalopod *Sepia* contains the phosphagen arginine phosphate,[48] while creatine phosphate has been identified in the muscle of several species of freshwater fish.[49] Arginine phosphate appears to play an important part in the metabolism of lobster and crab nerves.[50] The percolating filters used for water purification have a definite requirement of inorganic phosphate to ensure satisfactory functioning.[51–2]

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The isotope $^{32}P$ has no significant effect on the rate of biological oxidation in such filters[53] and they may be used safely for the removal of radioactive contamination from waste water.[54]

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## PHOSPHORUS AND INVERTEBRATES

### Insects

Insects contain the same organic phosphorus compounds as do other animals; adenosine triphosphate, for example, occurs in the muscles of flies as well as in those of frogs and rats.[1-2] There is a general increase in inorganic phosphate derived from organic combination during the metamorphosis of many insects, during nymphosis in *Lepidoptera*[3] and pupation in silkworms.[4] During emergence females of the butterfly *Deilephila euphorbiæ* excrete three times as much phosphate as males.[5] The total phosphorus content of grasshopper eggs remains constant during development, but pyrophosphate is high initially and inorganic phosphate increases.[6] The time of pupation of the flour beetle, *Tribolium confusum*, is proportional to the amount of phosphate in the food ration although this does not affect the total phosphorus content of the pupæ.[7] Phosphates may have an important rôle as buffer in the blood of insects.[8] Infestation of plants by insects, mites, aphids, etc., has in some cases been shown to be dependent on the mineral nutrition of the plant. Thus absorption of phosphorus by tomatoes is positively correlated with population of the mite *Tetranychus bimaculatus* infesting the plants,[9] while phosphorus deficiency of garden peas led to a reduction in the number of aphid progeny although deficient plants succumbed more readily.[10] A low supply of phosphorus to lemon seedlings did not, however, affect the red scale *Aonidiella aurantii.*[11] Administration of compounds of the radioactive isotope $^{32}$P to insects has proved a very efficient method of 'tagging' or labelling them for studies of subsequent movements.[12] Insects fed on sugar solution containing active phosphate show higher activity than larvæ reared in media or solution containing $^{32}$P.[13-4] When larvæ of the mosquito *Culex fatigans* were tagged by this method, the subsequent female adults were three times as active as the males.[15] The root maggot fly *Hylemya* sp. has been successfully tagged by applying a solution containing $^{32}PO_4$ to the soil around turnip plants.[16] Radioactive phosphorus is not suitable for labelling the plum curculio *Conotrochelus* owing to its short biochemical and radioactive half-life.[17] Phosphorus metabolism has been studied in the spider mite *Tetranychus bimaculatus* by means of $^{32}$P.[18] Treatment of insects with large doses of radioactive phosphorus may have adverse effects. Thus the fertility of houseflies is reduced by large doses of the order of 70–100 mC.,[19] while egg production is reduced in the wasp *Habrobracon juglandis* by doses above 50 μC./g.[20] and 28% of the resulting progeny are abnormal as compared with 1–2% in controls.[21] This effect on egg production is correlated with the number of $\beta$-particles received by the wasp during the first day after ingestion.[22] Sterility is produced in adult *Drosophila* treated with doses exceeding 5 μC./g.[23] Calculations show that $^{32}$P is 2·3 times as effective as *X*-irradiation in producing lethal mutations in this species, 18·8 mrd. (approx. 0·54 μC.) of $^{32}$P in the food of the larvæ being equivalent to 1000 r. of *X*-rays applied to the immature sperm.[24-5] The biological half-life of $^{32}$P in houseflies is about 0·8 day and in the cockroach *Blattella germanica* about 9 days for males and 14 days for females.[26] The jassid *Orosius* became labelled when fed on plants containing the isotope and 65% of the ingested $^{32}$P was excreted within 30 min. of the commencement of the feeding.[27] Radioactive phosphorus has been incorporated by synthesis into a number of organophosphorus insecticides which have then been used to study the absorption, translocation and distribution of the insecticide inside the insect body. These studies

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include parathion[28-9] and dimethyl-2,2-dichlorovinyl phosphate (DDVP).[30] Several studies have been of disturbances of phosphorus metabolism caused by insecticides with a view to elucidating their mode of action.[31] A refinement is the study of the distribution of radioactive phosphate in various metabolic intermediates in normal and poisoned insects.[31-4] Similar studies have been made on strains of flies susceptible and resistant to insecticides.[35] A correlation has been found between cholinesterase inhibition in insects and lability of the P–O aromatic bond in a series of 24 substituted phenyl phosphates.[36] Phosphorus metabolism has been studied during growth and metamorphosis of the wax moth *Galleria mellonella*.[37] Adenosine triphosphate acts as an intermediate in the activation of luciferin in fireflies.[38]

## Helminths

Infective larvæ of *Wuchereria bancrofti* have been labelled with $^{32}P$ by feeding the tagged host *Culex fatigans* on parasitized blood.[39] Similarly *Trypanosoma equiperdum* assimilated isotopic phosphorus from rats,[40] and the plant parasitic nematodes *Heterodera rostochiensis* and *Meloidogyne hapla* from tomato plants. Injury to the plants was not caused by interference with phosphorus metabolism in the latter case.[41]

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## PHOSPHORUS AND VERTEBRATES

### Occurrence and Distribution

Total phosphorus content is usually determined by the phosphomolybdate reaction after first destroying organic matter by oxidation.[1–4] Inorganic phosphorus is extractable by water. Schemes which have been developed for determination of the phosphorylated intermediates occurring in metabolizing tissue are based on the determination of phosphorus after fractionation of the tissue extract by various agents, and after acid hydrolysis for various times.[5]

It is difficult to give a precise value for the normal phosphorus content of animal tissues owing to great variations not only among individuals but also in the same individual at different times and under different environmental conditions. Provided a sufficiently large sample of normal individuals is tested a mean figure can, however, usually be obtained. Table I gives the normal phosphorus content of various animal organs, Table II that of human organs and tissues. In Table I the P values quoted for blood and other body fluids are for inorganic phosphorus, but for solid tissues total phosphorus data are given.

Phosphorus has been found to accumulate regularly in the human fœtus during gestation.[72] The rate of increase of phosphorus in the pig fœtus was 0·002 g./day during the first 2 months of gestation, rising to 0·0278 g./day during the 4th month.[73] In most mammals including man phosphorus tends to increase from birth[74] to a maximum at maturity and then to decline steadily to some constant value for the remainder of adult life.[6,8,57] Daily determination of the phosphorus content of muscle shows a rhythmic variation in the values with periods of 9 and 22 days.[75] It has been claimed that some of these variations are due to changes in the external environment such as the weather.[76] The total phosphorus of frog brain is three times as high in the summer as in the winter,[8] whereas that of rabbit muscle is lowest in summer.[76] Determination of the phosphorus content of blood taken from various vessels indicates that the highest concentration is in the portal vein and lowest in the renal vein.[77] The skeleton of the cow contains 83·57% of the total body phosphorus[78] and the calcium:phosphorus ratio of 1·7–1·8 is approximately the same for a number of species.[79] There seems to be no biologically significant concentration of calcium phosphate in the blood,[80] and although some workers have failed to demonstrate a relationship between calcium and phosphorus concentration in serum,[81] others claim some interdependence. Thus the average concentration product $\text{Ca} \times \text{P}$ is stated to be 25 in adult women[82] and 43·7 in children under 3 years.[56] The relationship between calcium, phosphorus and protein is stated to follow the equation: $\text{Ca} = -0{\cdot}255\ \text{P} + 0{\cdot}566\ \text{protein} + 7$ in nephritics.[83] A highly significant correlation is found between serum phosphorus and lecithin.[84] During the healing of fractures serum-phosphorus is observed to increase from 0·0037 to 0·005% in man[85] and from 0·003 to 0·004% in dogs.[86] A similar rise occurs, however, after surgery and is probably the result of shock.[87] The normal serum phosphate content is lowered in many diseases,[89–90] and increased by about 34% during epileptic seizures.[91]

**Refs. p. 1429**

*Table I.—Phosphorus Content of Normal Animal Tissues and Organs*

| Tissue | Species | P content % | Reference |
|---|---|---|---|
| Whole body | rat | 0·72 | 6 |
| Brain | frog | 0·20 | 7 |
| ,, | ,, | 0·19 | 8 |
| ,, | rabbit | 0·188 | 8 |
| ,, | ,, | 0·33 | 9 |
| Blood, whole | cow | 0·0066 | 10 |
| ,, ,, | ,, | 0·0043 | 11 |
| ,, ,, | steer | 0·0044 | 10 |
| ,, ,, | rabbit | 0·0045 | 12 |
| ,, ,, | sheep | 0·00185 | 13 |
| ,, plasma | cow | 0·0052 | 14 |
| ,, ,, | ,, | 0·0038 | 15 |
| ,, serum | ,, | 0·0074 | 16 |
| ,, ,, | ,, | 0·0056 | 17 |
| ,, ,, | dog | 0·0030 | 18 |
| ,, ,, | ,, | 0·00297 | 19 |
| ,, ,, | goat | 0·0065 | 20 |
| ,, ,, | horse | 0·0037 | 21 |
| ,, ,, | ,, | 0·0035 | 22 |
| ,, ,, | ,, | 0·00337 | 23 |
| ,, ,, | pig | 0·0085 | 24 |
| ,, ,, | ,, | 0·0083 | 25 |
| ,, ,, | rabbit | 0·0035 | 26 |
| ,, ,, | ,, | 0·00465 | 27 |
| ,, ,, | rat | 0·0077 | 28 |
| Cerebrospinal fluid | cow | 0·0032 | 29 |
| ,, ,, | dog | 0·00309 | 29 |
| ,, ,, | ,, | 0·00117 | 18 |
| Egg, white | guinea fowl | 0·06 | 30 |
| ,, yolk | ,, ,, | 0·17 | 30 |
| ,, shell | ,, ,, | 0·02 | 30 |
| ,, white | pigeon | 0·17 | 30 |
| ,, yolk | ,, | 0·58 | 30 |
| ,, shell | ,, | 0·02 | 30 |
| Egg, | frog | $6{\cdot}5 \times 10^{-6}$/100 eggs | 31 |
| Eye, vitreous | rabbit | 0·00069 | 32 |
| ,, aqueous | ,, | 0·00155 | 32 |
| Gastric juice | dog | 0·0025 | 33 |
| Glycogen | ,, | 0·72 | 34 |
| Liver | rabbit | 0·21 | 35 |
| ,, | ,, | 0·29 | 9 |
| Lymph, leg | ,, | 0·0025 | 36 |
| ,, liver | ,, | 0·0051 | 37 |
| Muscle | ,, | 0·169 | 9 |
| Optic nerve | cow | 0·016 | 38 |
| Saliva | dog | 0·011 | 39 |
| Skin | frog | 0·338 | 40 |
| Submaxillary gland | dog | 0·082 | 41 |

*Table II.—Phosphorus Content of Normal Human Tissues and Organs*

| Tissue | P content % | Type | Reference |
|---|---|---|---|
| Whole body | 1·12 | total | 42 |
| Brain, grey matter | 0·98 | ,, | 43 |
| ,, white matter | 1·8 | ,, | 43 |
| Blood whole, fœtal | 0·0037 | inorg. | 44 |
| ,, ,, new born | 0·0045 | ,, | 44 |
| ,, ,, ,, ,, | 0·0041 | ,, | 45 |
| ,, ,, ,, ,, | 0·0052 | ,, | 46 |

*Table II.—(continued)*

| Tissue | P. content % | Type | Reference |
|---|---|---|---|
| Blood, whole, children | 0·0049 | ” | 47 |
| ” ” ” | 0·00397 | ” | 48 |
| „ „ adult | 0·00379 | ” | 49 |
| ” ” ” | 0·00366 | ” | 50 |
| ” ” ” | 0·039 | total | 49 |
| ” ” ” | 0·0358 | ” | 50 |
| „ plasma, adult | 0·0029 | inorg. | 51 |
| ” ” ” | 0·0029 | ” | 52 |
| ” ” ” | 0·0082 | total | 51 |
| „ serum, new born | 0·006 | inorg. | 53 |
| „ „ children | 0·0054 | ” | 54 |
| ” ” ” | 0·0046 | ” | 55 |
| ” ” ” | 0·0042 | ” | 56 |
| „ „ adults | 0·0029 | ” | 55 |
| ” ” ” | 0·00375 | ” | 57 |
| ” ” ” | 0·00365 | ” | 58 |
| ” ” ” | 0·00375 | ” | 59 |
| „ leucocytes | 5·7 mg/$10^{12}$ cells | total | 60 |
| Cerebrospinal fluid | 0·00177 | inorg. | 61 |
| ” ” | 0·00175 | ” | 29 |
| ” ” | 0·0021 | ” | 62 |
| ” ” | 0·0012 | ” | 63 |
| ” ” | 0·00373 | ” | 64 |
| ” ” | 0·00145 | ” | 65 |
| Milk | 0·013 | total | 66 |
| ” | 0·014 | ” | 67 |
| ” | 0·005 | inorg. | 67 |
| Saliva | 0·0157 | ” | 39 |
| ” | 0·0161 | ” | 68 |
| ” | 0·0195 | total | 39 |
| ” | 0·0165 | ” | 68 |
| Sweat | 0–0·0048 | inorg. | 69 |
| Thymus | 3·57 | dry wt. | 70 |
| Thyroid | 1·38 | ” | 71 |

## Growth Requirements of Phosphorus

Much attention has been paid to the normal requirements of phosphorus for adequate growth and maintenance of health in man and animals and much of this earlier work has been reviewed.[92–4] The estimated daily requirements of phosphorus are: for man[95] 0·88 g./70 kg.; pigs[96] 6·5 g./100 lb. for body weight at 50 lb. weight falling to 4 g./100 lb. at 200 lb. body weight; sheep[97] 2·5 g./100 lb.; chickens[98] 0·5% of ration; dairy cattle[99–100] 10–12 g./100 lb. live weight. As important as, if not more important than, the phosphorus intake is the ratio of calcium to phosphorus in the diet. Thus the optimum ratio Ca:P for growth of pigs,[101] of man[102] and of chickens[103] is between 1 and 2. Administration over a long period of diets with a ratio outside these limits may result in severe rickets.[104–5] With a high Ca:P ratio, greater than 2·5, blood phosphorus may increase and tetany result, while a low ratio below 0·4 causes blood-phosphorus to fall and rickets to develop.[106] An excess of calcium in the diet tends to impair the retention of phosphorus in the body.[107] A retention of 40 mg. of calcium and 20–25 mg. of phosphorus per kg. per day is desirable for artificially fed infants, but for older children retentions of 10 mg. of calcium and 10 mg. of phosphorus are satisfactory.[108] A higher percentage of ingested phosphorus is retained by infants receiving human milk than by those on cow's milk.[109] There appears to be no difference in effects on reproduction, calcification and teeth formation if the calcium and phosphorus are supplied as inorganic salts rather than as milk and green vegetables[110] and the retention is equally good.[111] Retention of phosphorus is almost 100% from disodium hydrogen phosphate but is less from bone meal.[112-3] Dicalcium phosphate is superior to tricalcium phosphate as regards calcification when administered to poultry.[114] An excess of dietary phosphorus is regarded as the principal cause of 'slipped tendon' in chickens.[115] Rickets appears to be due to an unsuitable ratio of calcium to phosphorus in the diet in addition to a deficiency of vitamin *D*.[116] Vitamin *D* does not appear to have a direct action on the absorption in the intestines of phosphorus,[117] but it influences phosphorus retention through its action on the absorption of calcium.[118-9] It is of interest that irradiation of pigs with a carbon arc lamp increases both the calcium and the phosphorus retention.[120] Addition of phosphorus to the diet enhances the potency of vitamin D in assays.[121] Seasonal variations have been observed in the absorption and excretion of phosphorus.[122] Studies of the rate of absorption of phosphorus by rats using $^{32}P$ show that only 60% of the ingested phosphorus is absorbed and 20–30% of that absorbed is re-excreted within 8 hr.[123]

Diets containing an unsatisfactory Ca:P ratio can interfere with sexual maturation and cause irregularities in the reproductive cycle of rats.[124-5] The ratio of the two elements has a greater influence on calcification than have the absolute levels of either.[126-7] Inorganic phosphate is more important for calcification than organic forms such as phytic acid.[128] Although no direct connection can be demonstrated between dental caries and dietary levels of calcium and phosphorus, the incidence of caries is correlated with lowering of retention of both calcium and phosphorus.[129-30] An increase of sucrose in the diet of rats tends to raise the calcium and phosphorus contents of the enamel and dentine of the incisors.[131] A reduction in the intake of phosphorus causes an immediate fall in the blood phosphate content,[132] but this can be restored by supplementing the diet with inorganic phosphates.[133] An inverse relationship exists between calcium and phosphorus concentration in the blood[134] so that the product of the two concentrations tends to constancy.[56, 82, 135] The main factor controlling the absorption of calcium and phosphorus appears to be the acidity of the gastric juices.[136] Phytin labelled with $^{32}P$ appears to exchange its phosphorus readily after ingestion by turkeys without enzymic hydrolysis.[137] Large doses of iron salts increase the excretion of phosphorus in the intestines,[138] while ingested ferric phosphate is absorbed very poorly by the body compared with calcium dihydrogen phosphate.[139] Administration of disodium phosphate so as to maintain high blood phosphorus levels reduces the concentration of lead ions in the blood following lead poisoning.[140]

Early work on phosphorus deficiency in cattle has been reviewed.[141] An unmistakable symptom is a depraved appetite for wood, bones etc.[142-4] Growth and utilization of food are impaired[145] and after a considerable time the bones become soft owing to losses of phosphorus and calcium.[146-8] There may be an increased output of urinary nitrogen.[149] During recovery from a condition of phosphorus deficiency the turnover rate of phosphorus in the femurs of rats is very greatly increased.[150] The ash content of the teeth increases much more slowly than that of the bones.[151]

## Distribution and Exchange

The radioactive isotope $^{32}P$ has proved invaluable for studies of the distribution of phosphorus in animal bodies following administration by various routes. There is invariably a rapid rise in the phosphorus content of the blood plasma, but within 8 hr. this begins to fall as phosphorus is transferred to other cells and tissues.[152] Lower levels of plasma phosphorus occur in febrile patients owing to increased partition with cells.[153-4] The order of decreasing rate of uptake of circulating phosphate from the blood is liver, kidney, heart, spleen, lung, muscle, brain.[155] About 90% of the administered dose appears in the bones[156] although the specific activity is lowest owing to the greater phosphorus content.[152] The biological half-life of phosphorus in the human body is about 30 days.[157-8] The mean turnover rates of $^{32}P$ labelled phospholipids from the blood stream of dogs was 0·15 millimole/hr.,[159] and the half-life of phosphorus in the blood stream was 8 ± 1 days.[158] Such turnover studies have been used to deduce the mean life of leucocytes in patients with various blood diseases.[160]

The rate of transfer of phosphate through the red blood cell membrane is calculated to be 8·49 micromoles/min./l. of plasma;[161] this rate falls off rapidly with decreasing temperature.[162] The exchange has been attributed to slow diffusion[161] but active transport linked with metabolic processes also plays an important rôle.[163] This is shown by the partial inhibition of transfer after treatment with enzyme inhibitors such as iodoacetate and fluoride ions.[164] The rate of transfer of phosphate through the cell wall is also depressed by sodium oxalate,[165] and *X*-irradiation.[166] Red blood cells may be able to utilize adenosine in place of glucose for transporting phosphate through the cell wall.[167] Cerebrospinal fluid contains 60% of the diffusible calcium and 26% of the diffusible phosphorus of blood serum and cannot therefore be simply a plasma-ultra-filtrate.[168] The transfer coefficient of $^{32}PO_4$ through the capillary walls is $20 \times 10^{-3}$ in normal persons and is almost doubled in ascitic patients.[169] Adrenaline increases the rate of transfer of phosphorus from blood plasma to tissues.[170] The rate of uptake by skeletal muscles decreases during activity and increases during the recovery period.[171] Transfer of phosphate from blood stream to nerve cells is very slow,[172] equilibrium requiring some 10 days to become established.[173] The rate of equilibration throughout hen's eggs is, on the contrary, rapid.[174] Excised eye lenses rapidly take up $^{32}PO_4'''$ from solution,[175] the rate being the same in light or in darkness.[176] There is no evidence of a posterior–anterior concentration gradient through the lens but rather a 100-fold excess accumulates in the epithelium.[177] This difference disappears in cases of radiation cataract.[178] Equilibrium between blood stream and cornea is slow, requiring some 7 days, whereas penetration into the aqueous humor is due to simple diffusion and is much more rapid.[179] A complete exchange of phosphorus between blood stream and ocular tissues is calculated to require some 2000 days.[180] Penetration of phosphate ion through intact skin follows an exponential law with a half-period of about 2 hr.,[181] but the rate of penetration is greatly increased by irradiation or application of lanolin.[182] Although the attainment of equilibrium between the phosphate contents of the blood and the cerebrospinal fluid is rapid (1–3 hr.), some 5 days are required for cerebral tissues to come into equilibrium with the blood plasma[183] and the rate of entry of the $^{32}PO_4'''$ ion appears to be the limiting factor.[184] Applications to the brain tissue of electrical pulses cause a conversion of acid-soluble phosphate into an acid-insoluble form.[185] The uptake of phosphorus by bone is largely in the more recent, poorly mineralized regions, the epiphyses.[186–8]

Phosphorus atoms present in the teeth are readily exchangeable with those of the blood stream, even in those parts of the teeth remote from the pulp.[189] The exchange of $^{32}P$ atoms in the dentine is largely with the blood stream but enamel exchanges with saliva.[190] Exchange is more rapid in functioning teeth which are regularly used for chewing.[191] The dentine may be rendered impermeable to $^{32}P$ by the formation of a precipitated layer of calcium fluoride.[192] Autoradiographic localization of the phosphorus in the rat intestine after administration of $^{32}PO_4'''$ shows that a little is present as deoxyribosenucleic acid but the bulk appears to be free inorganic phosphate.[193] The ratio of the radioactivity of pleural effusion to that of blood plasma after injection of solutions containing $^{32}PO_4'''$ ions varies widely with different lung diseases.[194] Two minutes after the intravenous injection into rabbits of lipovitellin labelled with $^{32}P$ at least 25% is found in the lungs.[195] The maximum excretion of $^{32}P$ in bull semen, however, occurs about 14 days after injection.[196] The distribution of radioactive phosphate in frog embryos at different ages has been studied after inoculation of the egg with the isotope.[197] Phosphorus is largely present at the surface of the shells of eggs laid by hens fed with rations containing $^{32}P$.[198]

## Excretion of Phosphorus

There is a daily rhythm in the excretion of phosphorus by sheep[199] and by man.[200] In dogs[201] and man[202] about 10% of an orally administered dose of $^{32}PO_4'''$ is excreted in the first 24–48 hr. Starvation may increase the rate of excretion by rats more than 60 times the normal rate.[203] During work, after a preliminary rise, excretion practically ceases and is resumed only during recovery from work.[204] Between 40 and 60% of the phosphorus eliminated is excreted via the kidneys, the remainder via the fæces.[205-6] The correlation coefficient between the concentration of inorganic phosphate in the blood and the rate of excretion of the same form in the urine is $0{\cdot}416 \pm 0{\cdot}071$.[207] Studies of the relative specific radioactivities of the urine and blood after ingestion of a dose of $^{32}PO_4'''$ suggest that most of the inorganic phosphate of the blood plasma exists in a simple filterable state.[208] Elimination ceases when the blood-phosphate falls below a certain level, this threshold being changed by phlorizin, by uranium salts and by varying the ionic product $Ca \times P$ in the blood.[209] There is reabsorption of phosphate in the glomeruli; the mean value was $91{\cdot}3 \pm 3{\cdot}3\%$. Administration of hormone of parathyroid gland or enhanced activity of the parathyroid reduces this reabsorption and hence increases the rate of elimination.[210-2] Serum-phosphate remains at the normal level until the glomerular filtration rate falls below a certain value, when it begins to increase once more. Although the concentration of fæcal phosphate varies directly with fæcal calcium content, the urinary phosphate varies inversely with fæcal calcium and the phosphate of the milk.[214] All segments of the intestinal tract, but particularly the jejunum, appear to be important for the excretion of phosphorus.[215-6] Excretion *via* both kidneys and intestine is reduced when the diet contains copper and molybdenum ion in amounts of approx. 40–80 p.p.m.[217]

## Phosphorus Metabolism

### GENERAL

There have been recent reviews of present knowledge of the metabolism of phosphorus in man,[218] in animals[219] and in the eye.[220] There is some evidence that the adrenocorticotropic hormone (ACTH) controls the systems responsible for the transport of phosphorus across cell boundaries,[221] this action of ACTH being potentiated by ascorbic acid.[222] The effects of cold on the phosphorus metabolism of animals can be explained as an effect on the production of ACTH by the adrenals.[223] The activation energy of the exchange of phosphate between the red blood cells and plasma is 19·8 kcal./mole over the range 15·5–37·5°C. The transfer is an active transport process dependent on glycolysis.[224] Most of the organic phosphorus of red blood cells appears to be present as adenosine triphosphate (ATP).[225-6] Uptake of phosphorus by the lens of the eye and the incorporation into phosphorylated intermediates appear to follow a different pathway under the influence of inhibitors such as fluoride or cyanide.[227-8] After injection of $^{32}PO_4'''$ into laying hens the radioactive phosphorus can be detected in the yolks of the 2nd to the 7th eggs laid over a period of 10 days.[229] Yolk is the principal source of phosphorus compounds for the developing embryo.[230] Phosphorolytic enzymes of the glycolytic pathway are detectable in the chick embryo at the 23rd hr. of development.[231] The determination of phosphorus combined as deoxyribonucleic acid (DNA) has proved useful for the rapid estimation of the numbers of cells in a sample of tissue.[232] Through the use of $^{32}PO_4'''$ it has been found that the time cycle for cell division in human bone-marrow is 40–80 hr. while the period of DNA synthesis is 12–15 hr.[233] The phosphorus required for the synthesis of both cytoplasmic and nuclear ribonucleic acid and of deoxyribonucleic acid comes from the cytoplasm alone and not from the nucleus.[234]

One of the earliest applications of radioactive phosphorus was in the study of the metabolism of phospholipids in mammals. After feeding $^{32}PO_4'''$ with or without olive oil to rats, labelled phospholipids rapidly appear in many organs, such as liver, intestine, kidney, etc.[235-7] but more slowly in brain.[238] The lungs are particularly active in phospholipid synthesis and a single injection of phosphate and oil doubles the phosphatide content of the tissue while the specific activity of the lungs rises to 5 times that of controls not receiving oil.[239] The amount of phosphorus synthesized into phosphatides is larger than the amount of phosphate administered.[240] The phosphorus of phospholipids circulating in the blood does not appear to be drawn from the same source as the phosphate of urine.[241] The synthesis of phospholipids is accelerated by choline, the effect being proportional to the amount administered.[242-3] Acetylcholine is even more potent, stimulating the incorporation of $^{32}$P into choline-containing lipids by 400–600% and into non-choline-containing lipids by 1000–2500%.[244] Betaine is also active but less effective than choline.[245] The dietary protein level may also play an important rôle in the synthesis of phospholipids.[246] Coenzyme *A* increases the rate of incorporation of $^{32}$P into phospholipids if present below a certain concentration; otherwise the rate is decreased.[247] The adrenocorticotropic hormone (ACTH) increases the synthesis of brain phospholipids which are used up during periods of intensive brain activity, other phosphorus-containing fractions remaining constant.[248] There is some evidence that increased phosphorylation of lecithin is associated with mitosis of cells.[249] Studies of the rate of incorporation of $^{32}PO_4'''$ into ATP of muscle indicates that the terminal phosphorus atom is replaced 6–8 times faster than the middle phosphorus atom and 100–200 times faster than the innermost phosphorus atom.[250] The inorganic phosphate of muscle is used up in glycolytic processes during shock and application of high pressures.[251-2] The rate of incorporation of $^{32}PO_4'''$ into ATP has also been determined in brain tissue.[253] During excitation by drugs the rate of exchange of the phosphorus atom of ATP and phospholipids is increased.[254] Oxygen deficiency[255] and narcotic sleep[256] reduce the rate of exchange.

Recent work on the metabolism of phosphorus in bone has been reviewed.[257] Radioactive phosphorus has been used in such studies and although it appears to have no detectable interference with bone-healing processes[258] administration to pregnant mice has resulted in disturbances to osteogenesis and odontogenesis.[259] Calcium and phosphorus are laid down in the long bones in the ratio 2:1.[260] Calcium and phosphorus salts have the apatite lattice but their composition is variable and ranges from α-tricalcium phosphate to hydroxyapatite.[261] The ion-exchange properties of bone have been investigated and the rate-determining step in the exchange of phosphate appears to be the escape of phosphate ions from the crystal surface to the hydration shell.[262] Both beryllium ions and histidine inhibit calcification, but the exact mechanism is not clear[263] since phosphorus is utilized for ossification equally well from inorganic phosphate, phosphate esters, and ATP.[264] Fractionation of the phosphorus compounds present in ossifying cartilage indicates the major constituents to be orthophosphate and ATP.[265] The epiphyses acquire labelled phosphate from the blood stream at twice the rate for the diaphyses, but this difference is later reduced.[266] The actual mode of action of the anti-rachitic vitamins of the *D* group remains obscure. Part of their influence on ossification may be by regulating the absorption of calcium and phosphorus from the intestines,[267] and partly by facilitating the conversion of organic to inorganic phosphate.[268] They also appear to have some influence on the mobilization of skeletal phosphate.[269] Irradiation of guinea pigs with ultra-violet light results in increased calcium and phosphorus in the bones as well as in the whole organism.[270] Cortisone appears to be the only hormone concerned with bone repair.[271] An excess of phosphate does not influence the rate of normal bone healing,[272] During the healing of fractures in rats fixation of phosphate is small during the first 20 days but rapid in the following 10 days.[273] In bone transplants in rabbits depositions of phosphorus reached a maximum at 7–12 days and then declined.[274] The pathology of tetany has been explained as a disturbance of the equilibrium between the various phases of calcium phosphate resulting in an increase in the concentration of phosphate ions.[275] Increased feeding of phosphate had very little effect on the dentine of teeth.[276] The incorporation of $^{32}$P into nucleic acid increases greatly in vitamin *E* deficiency in rabbits.[277] The isotope is synthesized more rapidly into ribonucleic acid than into deoxyribonucleic acid.[278]

USE OF RADIOACTIVE PHOSPHORUS FOR DIAGNOSTIC AND THERAPEUTIC PURPOSES

The isotope $^{32}P$ has found considerable application in biology not only for the study of normal physiological and metabolic processes but also for the diagnosis and therapy of pathological conditions. There are available a number of general reviews.[279-82] Techniques range from the quantitative determination of the radioactivity taken up by tissues and organs using counting methods[283] to localization of the radioactivity inside tissues and cells by autoradiography.[284]

Red blood cells and lymphocytes labelled with $^{32}P$ have been used to study the biological life of the cells inside the animal body[285-9] and also to measure the total blood volume.[290-1] The phosphorus of the red blood cells in sickle-cell anæmia has a turnover time 2·5 times greater than that of normal cells.[292] Radiation effects of the $^{32}PO_4'''$ taken up by the cells may interfere with the experiment. Thus $^{32}PO_4'''$ produces changes in chicken blood that are not produced by *X*-irradiation, namely a great decrease in the eosinophils.[293] Lethal changes may be produced in cell nuclei[294] and gross histological changes in many tissues.[295] In a number of leukæmia patients the logarithm of the white cell count plotted against integral radiation dose from ingested $^{32}P$ was a straight line.[296] Considerable variations in response to small doses of $^{32}P$ may be found among different species. Thus rats have a much higher rate of elimination of $^{32}P$ than have guinea pigs.[297] The hen appears to be very resistant to radiation damage from ingested $^{32}P$,[298] but the developing chick embryo is very sensitive.[299] Administration of antibiotics reduced mortality in rats given lethal doses of $^{32}P$, by preventing invasion of the tissues by pathogenic microorganisms.[300]

The most useful application of radioactive phosphorus has been in the diagnosis and treatment of cancer. Recent work on these aspects has been reviewed.[301-7] Many forms of malignant tumour exhibit reduced respiration and an increased glycolytic activity which results in the increased metabolism of phosphorus.[308-9] The rate of turnover of phosphorus in deoxyribonucleic acid may be increased threefold in certain carcinomas.[310] This increased metabolic activity usually implies an increased uptake and concentration of radioactive phosphorus compounds in the tissue following administration of $^{32}PO_4'''$.[311] Care must be taken in assessing quantitative turnover rates since the virulent cells may take up phosphorus from dead cells.[312] Autoradiography shows that $^{32}P$ accumulates largely in the sarcoma cells of ascitic fluid withdrawn from mice inoculated with Yoshida sarcoma.[313] There is also increased uptake in meningiomas, metastic cancer, neuromas and especially in gliomas.[314] Diagnosis is considered significant if the activity of pathological sites is 25% greater than corresponding normal sites.[315] The relative concentration over normal in 13 histologically proved tumours varied from 0·9:1 to 34:1.[316] In malignant tumours of mammary glands the excess over normal varied from 21–600%, whereas in benign tumours the range was 0·1–11%.[317] Increased uptake of $^{32}P$ by eye tumours may or may not be observed[318-9] and a test is regarded as positive if the uptake in 1 hr. is 30% above normal and if the uptake continues to increase over 24 hr.[320] Uptake of $^{32}P$ by mammary tumours in female mice is significantly increased by œstrogens and decreased by testosterone.[321] Accumulation of $^{32}P$ in tumours is reduced by *X*-irradiation,[322] the reduction being largely in the DNA-phosphorus.[323] Since injected $^{32}PO_4'''$ is preferentially taken up by tumour tissues, it should act as an internally distributed source of radiation with the highest intensity at the required site.[324] The highest concentration of $^{32}P$ usually occurs in the bone marrow and in sites of leukæmic infiltration and the highest therapeutic success has accordingly been achieved in blood diseases such as leukæmia and particularly polycythæmia[325-6] although remissions usually occur in 2–5 years.[327-8] Other therapeutic applications of varying success include metastatic, peritoneal and pleural carcinoma, carcinoma of the breast, prostate, cervix etc.[329] The number of dead tumour cells present in ascitic fluid may increase by 100% after the ingestion of $^{32}PO_4'''$.[330] A small percentage of osteogenic tumours has been reported in mice treated with $^{32}P$ possibly attributable to the radiation effects.[331]

## PHOSPHORUS AND PROTEINS AND ENZYMES

Proteins have been labelled with $^{32}$P by treatment with phosphoryl chloride, but the reagent considerably modifies the properties of the protein.[332] Analysis of the ash of proteins shows that phosphorus is present in most if not all[333] of them. The heat coagulation of caseinogen appears to be related to dephosphorylation of the protein.[334] Careful enzymic hydrolysis of $\alpha$-casein shows that 40% of the phosphorus is present as the monoester, 20% as pyrophosphate and 40% as the diester.[335] An enzyme has been found in rat liver mitochondria which catalyzes the transfer of phosphate from adenosine triphosphate to proteins.[336] Other enzymes catalyze the exchange of phosphate from ATP to ribonucleic acid,[337] to glycerol,[338] and in many other phosphorylations for the study of which radioactive phosphate has been found a valuable tool.[339–40]

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### SECTION XL

# THE TOXICITY OF PHOSPHORUS COMPOUNDS

BY A. F. CHILDS AND H. COATES

## Introduction

PHOSPHORUS and its compounds show a very wide range of toxicity. On the one hand orthophosphates are a major component of the skeletal tissue of many animals, and play an essential part in the biochemistry of both plants and animals (see Section XXXVIII). On the other hand white phosphorus and certain of its inorganic compounds (phosphine, and phosphides yielding phosphine on hydrolysis) have a high toxicity. The organic compounds of phosphorus exhibit a similar variation, some being without apparent physiological effect at very high doses, while others are among the most toxic synthetic materials known to man.

## INORGANIC PHOSPHORUS COMPOUNDS

### Phosphorus

Toxic phenomena due to the ingestion or inhalation of elemental phosphorus are virtually confined to white (yellow) phosphorus. The amorphous polymeric allotropes (red phosphorus) are generally considered as almost non-toxic, although there have been suggestions of a toxicity not due to residual untransformed white phosphorus.[1] No detailed reports of the toxicity of the other phosphorus allotropes have appeared.

#### CHRONIC PHOSPHORUS POISONING

The most common symptom of chronic poisoning by the ingestion or inhalation of white phosphorus is a form of bone necrosis or osteomyelitis, which since it appears mainly in the upper and lower jaw has been known for many years as 'phossy jaw'.

The first cases of phossy jaw arose in Vienna in 1839 following the use of white phosphorus in the match industry. Commercial manufacture of red phosphorus started in 1851, and with its application in the match industry (1855), followed by the alternative use of phosphorus sesquisulphide (1898), and the prohibition of the use of yellow phosphorus in matches by the Berne Convention of 1906, the incidence of phossy jaw has declined to negligible proportions. The disease is now indeed largely confined to factories manufacturing elemental phosphorus, though there was a minor recrudescence of the condition associated with the use of white phosphorus in the manufacture of fireworks during the first decades of the 20th century.[2] With legislation against the indiscriminate use of white phosphorus, and marked improvements in manufacturing plant ventilation and the oral and dental hygiene of workers, such cases as now occur are usually very mild[3-4] in comparison with earlier observations.[5-6]

The condition usually starts with toothache and local inflammation, or a generalized dull and lifeless appearance of the gum, which is followed by rupture of the surface and a discharge. Even if the tooth is extracted the cavity is slow to heal, and exudes pus. Treatment by antibiotics usually controls this, and the lesion becomes sterile. In either case a small sequestrum of bone may separate, as a spongy mass similar in appearance to pumice stone.[3] Under the influence of antibiotics the lesion is almost dry, and the healing, though still somewhat slow, is uneventful with little or no permanent disability, except the loss of natural teeth in the areas involved. The sequestra differ from those in staphylococcal osteomyelitis in being light in weight, spongy, and yellow or brown in colour, rather than hard and well calcified.

The cause of phosphorus necrosis is almost as obscure as when the disease was first described[3]; indeed, it is not even certain whether the causative agent is white phosphorus itself or one of its lower oxidation products. Arsenic, a common minor constituent of phosphorus, caused a similar necrosis when used in dentistry to kill the roots of teeth, but since the disease is unknown in arsenic smelters, arsenic is not likely to be involved in phosphorus necrosis. It was, and is still, believed that the jaws are affected because of direct exposure to the fumes, which encourages subsequent attack by pathogenic organisms present in the mouth. However, there is considerable evidence that the disease is systemic in nature. Thus the condition usually requires a long induction period for its onset, e.g., 10 months to 18 years,[3] 7 weeks being the minimum reported,[8] and it may appear long after exposure to phosphorus has ceased.[8–9] Further evidence for the systemic nature of the malady is given by delayed healing after an iliac crest biopsy, done in order to investigate the relation of phosphorus necrosis to general bone metabolism.[3] There are also frequent early references to the fragility of the bones of some phosphorus workers,[6,10–1] though these were not borne out by a later study.[3] One case of extensive necrosis and malformation of the bones of the foot, following a deep and untreated phosphorus burn, has been described.[7]

Study of the disease is made more difficult by its low incidence. A recent author states that less than 5% of those exposed were affected,[5] while other estimates were even lower.[6,12] No systematic difference of any kind was found in the incidence of general infections, bone fractures, hæmatological findings or biochemical studies of blood and urine, between two groups of healthy workmen, one exposed to phosphorus and the other not. There were, however, significant differences between the two groups in the appearance of the dental tartar and the interior surface of the mouth.[3] Unlike acute phosphorus poisoning the chronic condition causes no apparent liver disease.[13]

Acute phosphorus poisoning in growing animals causes zones of increased density in the epiphyses of the long bones, and a reduction in the process of tubulation in the shaft, said to be due to diminished resorption of cartilage matrix and bone.[14] Significant bone changes are caused by administration of 0·05 mg./kg./day of white phosphorus, a dose well below the lethal one,[15–6] though these can be reversible in mild cases.[18] This has suggested that chronic phosphorus poisoning acts in a similar way by interfering with the blood supply to the bone, thereby rendering it more liable to infection, but no sound experimental evidence exists for this widely held theory. Some parallels can be drawn between phossy jaw and the radiation-induced necrosis suffered by luminous dial painters, and this and other evidence has been adduced in favour of a free radical mechanism for the bone and tooth damage caused by chronic white phosphorus poisoning.[16]

The present maximum allowable concentration of phosphorus vapour in air accepted in Britain is 0·1 mg./m.$^3$ This is based on animal experiments,[19–20] but the finding that fatty infiltration of the livers of rats exposed for a total of 30 hr. to phosphorus vapour could be caused by as little as 2·8 mg./m.$^3$ suggests that the figure might be reduced[16] perhaps to the level of 0·04 mg./m.$^3$ recommended in the U.S.S.R.[21] In any case a maximum allowable concentration cannot be meaningfully defined except in terms of an analytical method capable of determining white phosphorus vapour in air separately from its oxidation products.[16–7]

Prophylactic measures against chronic phosphorus poisoning include improved ventilation of working areas, medical (especially dental) examination of employees exposed to phosphorus, and removal from exposure of all those showing symptoms of the disease.[4,13]

### ACUTE PHOSPHORUS POISONING

Because of the use of white phosphorus in rat poisons, and in pharmacological preparations of various kinds,[12,22] fireworks,[2] attempted suicide[23] and deliberate administration in other ways,[25-6] much is known of the pathology of phosphorus poisoning. The clinical picture of acute phosphorus poisoning is well described by Mellor (VIII, 794). As little as 8 mg. of phosphorus has been reported to cause acute toxicity and death in man, but the fatal oral dose is normally considered to be of the order of 100 mg. ($1\frac{1}{2}$ grains),[13] and one case has been reported of recovery from a dose of 130 mg.[27] In 56 cases of attempted suicide the mortality was 48%, and the toxicity appeared to be increased by alcohol.[23] One fatal case of acute phosphorus poisoning showed a progressive fall in total urinary nitrogen excretion and high values for $\alpha$-amino nitrogen, probably due to kidney damage.[24]

Phosphorus appears to be equally poisonous to other animals. The effect on rats has been mentioned above and cases of poisoning in cattle,[28] pigs,[29] and waterfowl (ducks)[30] have been described. The median lethal concentration of phosphorus in water for fish (Bluegill, *Lepomis macrochirus*) lies between 0·025 and 0·105 mg./l., but death is due to colloidal phosphorus solutions, and not to the small concentration in true solution.[31] The median lethal oral dose for the American cockroach (0·02 mg./g.) was lower than that for the German variety (0·13 mg./g.).[32]

In mammals, including man, the main pathological lesion is fatty infiltration of various organs, particularly the liver, but also the kidney and the heart. Liver glycogen becomes depleted in the periphery of the lobule, followed by peripheral fatty infiltration and necrosis.[33] In rats this fat deposition appears to be associated with splanchnic stimulation and adrenaline activity, since it can be prevented by cutting the spinal cord above the tenth thoracic vertebra.[34] The liver damage can be detected by an impaired ability to metabolize blood acetone[35] or levulose,[36] and to synthesize glucuronic acid.[37]

Marked histological changes take place in the affected liver,[38] heart[39] and brain, though the last shows no fatty degeneration.[40] In the blood, red and white cell counts fall, sometimes after a fleeting increase, as do platelets, serum protein and hæmoglobin.[41-3] Studies with radioactive white phosphorus show high concentrations in the heart, spleen, and blood, as well as the liver and kidney,[44] the distribution in mice, rats, and rabbits being almost identical with that in humans.[45]

The treatment of acute phosphorus poisoning has received much attention. Where the poison has been taken by mouth early emesis or repeated stomach washing is of great value.[46] The oral administration of 0·1–0·2 g. of copper sulphate in 1% solution, or of 0·1% aqueous potassium permanganate solution, is also indicated. The patient should be given a diet high in protein and carbohydrate and low in fat.[26] The worst consequences of liver failure may be avoided by massive transfusions of blood,[76] vitamins (including vitamin-*K*),[43,52-4,56] glucose, fructose, and methionine.[47,55] Adrenal cortex extracts,[51] Mn(II),[57] methylthiouracil,[48] thyroxine[49] and carbanil,[50] have also been claimed to have therapeutic activity.

Because of its spontaneously inflammable character, white phosphorus is a common cause of skin burns. These are primarily thermal, but are aggravated by the toxic action of phosphorus itself and its oxidation products. The burning phosphorus must be immediately extinguished by water or sand, care being taken not to spread it. The remaining portions of phosphorus are then treated with 1–2% copper sulphate solution, to coat them and prevent their reignition,[59-63] and removed mechanically by scraping with a spatula or blunt knife, residual phosphoric acid being neutralized by treatment with 5% sodium bicarbonate solution.[58] Solvents for phosphorus, such as oils or fats, merely spread it and should be avoided. Other bases which have been employed in the later stages of treatment include magnesium hydroxide[64] and sodium percarbonate.[65]

## Phosphine

Phosphine is a very poisonous substance, and because it may be formed during a number of industrial operations there are many reports of cases of poisoning, including some deaths. Phosphine has been reported as a hazard in acetylene manufacture from calcium carbide containing phosphide[66-7]; in the use of aluminium phosphide as a grain fumigant[66,68]; in the treatment of phosphorus with alkali, especially during the manufacture of hypophosphites[69]; in the machining of metals such as cast iron[70]; and particularly in the handling of phosphorus-containing ferrosilicon.[66,71-2] In the last case grades of ferrosilicon containing 15–30% and 75–80% silicon are considered safe, the greatest hazard arising from a grade containing 30–45% silicon.[73]

Symptoms of acute phosphine poisoning may be of three types; firstly nervous disturbances, including headache, vertigo, tremors, and unsteady gait, leading in severe cases to convulsions, coma and death; secondly gastro-intestinal symptoms, including loss of appetite, thirst, nausea and vomiting, diarrhœa and severe epigastric pain; thirdly respiratory disorders such as oppression and pain in the chest and shortness of breath.[68-9,74-5] A characteristic but seldom-mentioned symptom is a sharp fall in blood pressure.[76] There have been suggestions of chronic effects, including anæmia, bronchitis, and gastro-intestinal, speech, and motor disturbances, from continued exposure to low concentrations,[75] though these are by no means general. Unlike arsine, phosphine does not cause hæmolysis of red blood cells.[69]

The following table showing the effects of phosphine on man has been compiled[67] and appears to be generally accepted.

*The Action of Phosphine on Man*

| Effect | Concentration | |
|---|---|---|
| | mg./l. | Parts per million |
| Rapidly fatal | 2·8 | 2000 |
| Death follows ½–1 hr. exposure | 0·56–0·84 | 400–600 |
| Dangerous to life after ½–1 hr. | 0·4–0·6 | 290–430 |
| Maximum exposure for ½–1 hr. without serious effects | 0·14–0·26 | 100–190 |
| Serious effects after several hours | 0·01 | 7 |
| Limit of perceptibility | 0·002–0·004 | 1·4–2·8 |

Two deaths were reported among the crew of a barge carrying ferrosilicon, a concentration of 5·9–6·1 p.p.m. phosphine being reported in the hold, and 1·0–2·0 p.p.m. in the crew room.[72] Fatal poisoning was also reported to result from daily exposure over several hours to 6·9–9·4 p.p.m.[77] However, several cases showing mild symptoms recovered without any apparent after-effect from transient concentrations as high as 35 p.p.m. The authors concluded from their observations that phosphine may not be as severely toxic as had been previously reported,[68] and this seems to concur with a subsequent relaxation of the maximum allowable concentration from 0·05[74] to 0·3 p.p.m. (ACGIH (recommended)).[75] However, it should be noted that even this higher value is below the limit of perceptibility by smell, and chemical means of detection should always be used where the presence of phosphine is suspected.[74] This is reinforced by the discovery that the odour-producing fraction of phosphine can be preferentially absorbed by various materials, leaving very high concentrations of the gas in the atmosphere without any detectable odour.[78]

The biochemical mechanism of phosphine poisoning is obscure, but it is known that the respiration of isolated liver mitochondria and isolated sarcosomes of the heart muscle in rats is affected. Sarcosomal respiration and phosphorylation are uncoupled. The respiration of *Neurospora crassa* is also affected, and this appears to be a general effect in living cells. Chronic administration of phosphine causes a similar effect in mitochondria at doses well below the toxic level.[79]

## Phosphides

Apart from the specific toxicity of the particular metal concerned, phosphides are normally toxic in so far as they evolve phosphine on hydrolysis by water or acids. In practice this behaviour is restricted to the phosphides of metals in the first three groups of the Periodic Table,[66, 80] and in particular to those of zinc, sodium, calcium, magnesium, and aluminium, which have been extensively used commercially as rodenticides, insecticides, and fumigants, and in marine signals.

Zinc phosphide, $Zn_3P_2$, has been used as a rodenticide since the second world war.[81-2] A review in 1947 pointed out its potential toxicity to man[83] and a number of cases of poisoning, accidental or deliberate, have been reported due to its use.[84-8] A review of 20 cases of this kind showed that the minimum dose to have caused death was 4–5 g., whilst a 50 g. dose had been survived. Dosages in the region of 100 mg. daily appear to be harmless.[89]

Early symptoms after ingestion of zinc phosphide include nausea, abdominal pain, chest tightness, excitement and agitation, and a feeling of chill. Vomiting is usual, and if it can be induced sufficiently early the chances of survival are increased. Death appears to arise from pulmonary œdema or cardiac damage, whilst those alive after three days recover completely.

Animal studies have shed some light on the mechanism of poisoning by zinc phosphide. Rats fed zinc phosphide in excess of the $LD_{50}$ ($40{\cdot}5 \pm 2{\cdot}9$ mg./kg.[82]) rapidly died, and phosphine could be detected in the expired air during life,[90] and in the liver during autopsy.[91] In lower doses there was good evidence, both in rats, and (in one case) in man, that zinc phosphide itself was present in the blood and the liver. It was assumed that some of the particles in commercial zinc phosphide were sufficiently small ($0{\cdot}1\ \mu$) to pass through the intestine wall into the blood stream.[91] This and other evidence was taken to prove that evolved phosphine is responsible for early symptoms, but that absorbed zinc phosphide particles give rise to the more usual delayed illness.[89]

Zinc phosphide has been shown to be toxic by inhalation,[84] percutaneous absorption,[92] and parenteral injection,[93] as well as by oral ingestion. It is also known to be toxic to sheep (LD 60–70 mg./kg.[94]), fowls ($LD_{50}$ 7–17 mg./kg.[95]), and pheasants ($LD_{50}$ 9 mg./kg.[96]), as well as to many game animals.[97]

Much less is known of the toxicity of other phosphides. A fatal case of poisoning by swallowing a proprietary composition containing 75% of $Ca_3(PO_4)_2$ and 25% of $Ca_3P_2$ has been described. It appeared to be due to the phosphine evolved.[88] Aluminium phosphide has been extensively used for the fumigation of bulk wheat supplies without apparently causing any cases of direct poisoning, though there is no reason to assume that it is intrinsically any less toxic than calcium phosphide.[68] Iron phosphide (ferrophosphorus), a major by-product of the manufacture of phosphorus and used extensively in the steel industry, is unreactive with water or acids, and no cases of poisoning by it have been reported.

## Phosphorus Oxides

Phosphorus pentoxide does not appear to have any specific toxic action towards mammals except that which would be expected from its highly exothermic hydrolysis to form the strong mineral acid, phosphoric acid. Dusts and smokes containing phosphorus pentoxide are formed during the commercial manufacture of phosphorus and phosphoric acid, and these irritate mucous surfaces, the eyes, and skin.[69, 75] However, the incidence of pulmonary disorders is not increased by chronic exposure to phosphorus pentoxide smokes arising from phosphorus furnaces, a behaviour in sharp contrast to that of the common oxides of nitrogen and sulphur.[76] The maximum allowable concentration in air (AIHA Guide) is 1 mg./m.$^3$ air,[69] while in the U.S.S.R. a lower desirable level is set (0·15 mg./m.$^3$ (instantaneous max.) and 0·05 mg./m.$^3$ (average/day))[98] (see also ref. 99).

The solid oxide can cause serious burns on the skin, because of its heat of hydration, and coagulation of skin protein by the phosphoric acid formed. For this reason it should always be washed off by copious quantities of water, followed by 5% aqueous sodium bicarbonate solution. One case of death has been reported from swallowing the solid oxide.[100]

No toxicological data have been reported for the other oxides of phosphorus, though they are assumed to behave similarly to the pentoxide.[75]

## Phosphorus Sulphides

Phosphorus sesquisulphide (tetraphosphorus trisulphide) was used to replace white phosphorus in the manufacture of matches in the belief that it was non-toxic. This appeared to be confirmed by experiments on dogs and man.[101] However the commercial sulphide can contain free phosphorus,[67] and more recently oral administration of the sesquisulphide in rabbits has produced histological changes similar to those produced by white phosphorus, but not entirely explicable by the amount of that substance present as impurity.[102] Nevertheless the acute oral toxicity of the substance must be relatively low.[69]

The most characteristic physiological action of the sulphide is the irritation caused by the dust on the lungs, eyes, and skin.[69] Affected eyes show symptoms of conjunctivitis of varying severity ('sesqui sore-eye'), but this normally disappears without apparent after-effect a day or so after removal from exposure.[76] The skin may show eczema, often referred to as 'match-box dermatitis', since it is commonly found on the skin of the thigh near to trouser pockets in which boxes of 'strike-anywhere' matches are carried. It may also occur on the hands, arms and face of workers handling the sulphide, those with oily skins being more susceptible. The affected skin becomes irritated, inflamed and rough, and in severe cases blisters may form.[104] Sensitivity of this type is by no means universal, and in many cases an allergic reaction having a delayed onset appears to be involved.[104-7] Indeed some authorities have associated the condition with the presence of chromium compounds in the match heads, rather than the sulphide itself,[103] but on the whole there seems little doubt that the sulphide is the allergenic agent in most cases.[108] No maximum allowable concentration has been set for the sesquisulphide.[69]

Phosphorus pentasulphide (tetraphosphorus decasulphide) hydrolyzes to hydrogen sulphide and various thiophosphoric acids. It is therefore strongly irritant to the upper respiratory and pulmonary tissue, as well as having a high systemic toxicity. The maximum allowable concentration (ACGIH threshold limit value) is 1 mg./m.$^3$ of air.[75,109-10]

## Phosphorus Halides

Phosphorus halides as a general class show the corrosive action one would expect from acids produced by hydrolysis. The skin, eyes, mucous membranes and lungs are all attacked, the severity depending on the concentration, time and facility for hydrolysis. Direct contact with the neat liquid can cause severe and often deep-seated burns.

### PHOSPHORUS TRICHLORIDE

Even though it is initially less soluble in water phosphorus trichloride appears to give more immediate symptoms than does phosphorus oxychloride, which tends to warn the affected person to leave the contaminated area before the lungs have been seriously affected.

Phosphorus trichloride has a pungent irritating odour resembling hydrogen chloride. It causes a feeling of suffocation, difficulty in breathing, lachrymation, bronchitis, œdema and inflammation of the lungs, and in severe cases a frothy bloodstained sputum. A concentration of 600 p.p.m. is lethal in a few minutes, while 50–80 p.p.m. can be harmful after 30–60 min.; 2–4 p.p.m. can be borne for up to 60 min. without serious symptoms, while 0·7 p.p.m. is the maximum tolerable for exposures of several hours.[74, 111–2] The maximum allowable concentration (TLV, ACGIH (recommended)) is 0·5 p.p.m.[75] Several cases of industrial poisoning by phosphorus trichloride,[113] including one fatal occurrence,[114] have been described.

Phosphorus trichloride is very aggressive to the skin and must be removed by washing with copious quantities of water.[115–6]

### PHOSPHORYL CHLORIDE

Because its immediately irritant effect is smaller, phosphoryl chloride vapour has a more insidious and dangerous effect than phosphorus trichloride. Inhalation causes pain in the throat and coughing, with burning and redness of the eyes. After a delay of 2–12 hr. secondary symptoms of lung damage may appear, including shortness of breath, coughing with bloodstained sputum, bronchitis, asthma, and emphysema.[67] Heart damage may occur. The condition resembles, but is normally milder than, phosgene poisoning.[117]

Various cases of poisoning by phosphoryl chloride have been described, both acute and chronic.[118–21] In general the patient should be treated as for phosgene poisoning, being removed to the fresh air, given artificial respiration if necessary, and kept warm. Inhalation of an aerosol of sodium bicarbonate solution with procaine, calcium to strengthen cell membranes, and penicillin against infection, has been recommended,[122] but nowadays penicillin or broad spectrum antibiotics, to combat secondary infection and treatment for pulmonary œdema, possibly including intermittent alcohol inhalations, together with treatment for the bronchial spasm, would be the treatment of choice.[76] Inhalation of ammonia, on the other hand, although it may allay irritation may worsen the clinical effects, and is not advised.[123]

### PHOSPHORUS PENTACHLORIDE

Phosphorus pentachloride has a pungent, unpleasant odour and its vapour or fume is irritant to mucous tissue, including the lungs. Hydrolysis of the pentachloride yields phosphoryl chloride, and massive exposure can give symptoms of poisoning by the latter.[67] However, because of its lower volatility it is less toxic, so long as it is not present as a particulate cloud, and the maximum allowable concentration recommended by the ACGIH is 1 mg./m.$^3$ air.[75]

### OTHER HALIDES

The other halides and oxyhalides of phosphorus, including the lower alkylphosphonic chlorides,[123] have a similar physiological action to the chlorides. Those containing fluorine hydrolyze to hydrogen fluoride as well as the appropriate phosphorus oxyacid, and therefore may cause the lesions of the skin and upper respiratory tract characteristic of poisoning by hydrogen fluoride.[75, 112] The bromides similarly yield hydrogen bromide on hydrolysis and are also very poisonous.

Thiophosphoryl chloride is a particularly insidious substance. The vapour, which has an odour somewhat resembling camphor, is not immediately aggressive, and it is possible to inhale a dangerous or even lethal dose without initial discomfort. Symptoms resembling those of phosphoryl chloride poisoning, particularly conjunctivitis and photophobia, may appear after a latent period of 2 hr. or more.[76, 114] The toxicity of thiophosphoryl chloride to rats by inhalation is somewhat higher than that of phosphoryl chloride.[124] Alkylthiophosphonic halides and the lower phosphonitrilic chlorides also have pleasant characteristic smells, but cause similar delayed effects to thiophosphoryl chloride.

## Phosphoric Acid and Phosphates

### PHOSPHORIC ACID

Phosphoric acid is less toxic than many other mineral acids, but being a strong acid, it can cause skin burns in some individuals if applied in concentrated solution.

No systemic effects have been reported, and although disturbances of breathing can be caused by inhalation of a phosphoric acid aerosol, the chance of œdema or other severe injury to the lungs is remote. Contact with the eyes may produce irritation or burns, but no permanent damage is to be expected. Flushing with copious amounts of water is the best treatment for both skin and eye contact. The threshold limit value (MAC), recommended by the ACGIH, is 1 mg./cu. m., although the vapour pressure is so low that this is not likely to be reached at room temperature except in an aerosol or spray.[75,125]

The phosphorus essential to the metabolism of all living things is ingested and transported mainly in the form of inorganic orthophosphate. This, and derived organic phosphates, are concerned with the structure of bone, the cyclic metabolism of carbohydrate, and the regulation of calcium level and acid/base equilibrium in body fluids. It is not surprising, therefore, that phosphate at reasonable concentrations has little pharmacological effect,[126] the normal plasma level being regulated at 3–4 mg./100 ml. in adults by the action of the parathyroid hormone.[12,127] Phosphate ion is not readily absorbed by the gastro-intestinal tract, and if large amounts are administered the quantity remaining unabsorbed gives rise to a mild cathartic action.[12] However, massive oral doses of mono- or disodium phosphate have been shown to cause kidney damage in young rats, including calcification and necrosis of the cells of the convoluted tubules,[128–30] as well as calcification of other tissues, such as the stomach and aorta.[127] While some workers have fed rats with food containing up to 1·30% of phosphorus without causing apparent ill effects,[131] others have observed signs of calcification in the kidneys of rats on a diet containing as little as 0·71% of phosphorus.[132] The effect is obviously dependent on other dietary components.

Sodium phosphate in moderate doses acts mainly as an indifferent saline when injected intravenously, but large doses (0·7 g./kg.) injected into dogs cause tetany, due to a major fall in blood calcium level. Phosphoric acid produces a similar fall of calcium without tetany.[126,12]

The absorption of calcium and phosphate by the intestine is linked, large amounts of either interfering with the absorption of the other by formation of insoluble calcium phosphate,[126] though moderate amounts are without effect.[127] For communities with a low calcium intake 30 mg/kg of phosphate is acceptable as a total dietary intake of phosphate. Where calcium is high this can be raised to 70 mg./kg.[133] The long-continued daily intake of 5–7 g. $NaH_2PO_4$ is without adverse effects in man.[134] The calcium and phosphorus intake of domestic animals can be increased by feeding dicalcium phosphate ($CaHPO_4$) often in the form of defluorinated apatite. The F/P ratio in such cases should be less than 0·025.[135] Calcium phosphate (2–3%) has also been suggested as a means of killing pests of stored grain.[136] Chromic phosphate (2·0 mg./g.) was lethal to rats on intravenous injection, possibly because of the chromium content.[137]

Slight pathological changes which have been observed in the skeleton and upper respiratory passages of workers engaged in superphosphate manufacture have been generally ascribed to the hydrogen fluoride evolved in this process.[138–40]

### DIPHOSPHATES (PYROPHOSPHATES)

Diphosphate is formed from adenosine triphosphate by enzymatic reactions, and itself takes part in phosphorylation reactions or is hydrolyzed to orthophosphate. Ingested diphosphate is excreted as orthophosphate.[127]

High concentrations (>1%) of diphosphate administered orally cause kidney calcification similar to that from orthophosphate, the effect of a given dose being slightly more severe. Larger doses cause hypertrophy and hæmorrhage of the stomach,[141] probably due to hydrolysis and resulting acidification. These effects are not likely to occur in the concentrations at present used in food products, and the acceptable daily intake of pyrophosphate for man can be calculated simply on the basis of its contribution to the total orthophosphate intake.[127]

### POLYPHOSPHATES

Because of their application in the detergent and food processing industries, pentasodium triphosphate and higher polyphosphates have been the subject of extensive toxicological studies, reviewed by a number of authors.[127, 142–6] If taken orally the polyphosphates are not absorbed as such to any significant effect, but only in the form of orthophosphate to which they are hydrolyzed, possibly in part by the intestinal flora. In spite of its powerful sequestering action, 'sodium hexametaphosphate' (Graham's salt) has no effect on the absorption or utilization of calcium[148] or iron[149] by rats. The acceptable oral intake of polyphosphates can be related to the total dietary phosphate as if they were all hydrolyzed to orthophosphate. The calcification and necrosis which they cause to kidney tissue are similar to those from orthophosphate.

The intravenous toxicity of condensed phosphates is higher than their oral toxicity. Thus a commercial preparation consisting of $\frac{1}{3}$ Kurrol's salt and $\frac{2}{3}$ mixture of disodium and tetrasodium pyrophosphate had a median lethal dose in rats of 4000 mg./kg. body weight. Intravenously the $LD_{50}$ was 18 mg./kg. Calcium phosphate incrustation of the kidney tissue was evident even at 1% level in diet, and damage increased above this dose level.[142]

The following toxicological data have been recorded for the mouse[147]:

*Median Lethal Dose* ($LD_{50}$) *g./kg.*

| Compound | By route | | |
|---|---|---|---|
| | Oral | Subcutaneous | Intravenous |
| $Na_2H_2P_2O_7$ | 2·65 | 0·48 | 0·059 |
| $Na_4P_2O_7$ | 2·90 | 0·40 | 0·069 |
| $Na_5P_3O_{10}$ | 3·21 | 0·90 | 0·071 |
| $Na_6P_4O_{13}$ | 3·92 | 0·875 | — |
| Graham's salt | 7·25 | 1·30 | 0·062 |
| (cyclic) $Na_3P_3O_9$ | 10·30 | 5·94 | 1·165 |
| (cf. NaCl) | 5·89 | 3·00 | 0·645 |

### OTHER PHOSPHORUS OXYACIDS

Sodium hypophosphite has been taken orally for many years as a component of various 'tonics' without apparent ill effect, except possibly headache, vertigo and colic, resulting from overdose.[150] Hypophosphites are excreted rapidly, and almost completely unchanged.[12] Hypophosphorous acid also has a low toxicity, although as a strong acid its concentrated solution must be handled with care.[100]

Very little is recorded of the toxicity of phosphites, but it appears to be of the same order as that of hypophosphites, since phosphites show a negligible or low-order toxicity in rats, and cause little interference with enzyme activity.[151]

Nothing is known of the toxicity of hypophosphates. Aqueous solutions of the free acid cause blistering of the skin, which may take several days to appear, and is slow to heal. They also cause severe eye damage.[152]

Both monofluorophosphoric acid and hexafluorophosphoric acid are highly corrosive liquids, with an effect on the skin or eyes reminiscent of that of hydrogen fluoride.[75]

Rats fed diets containing up to 0·34% of $Na_2PO_3F$ showed no changes in the liver, spleen or adrenals, but histological changes in the kidney indistinguishable from those caused by the administration of similar quantities of sodium fluoride. The data indicated that the toxicities of sodium monofluorophosphate and sodium fluoride are of the same order.[153] Experiments with $^{18}F$ and $^{32}P$ labelled sodium monofluorophosphate revealed high concentrations of $^{18}F$ absorbed in the intestinal lumen and the liver and of $^{32}P$ in the intestinal wall, as compared with the same isotopes in the form of fluoride and orthophosphate ions, respectively.[154]

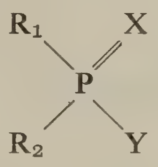
The monofluorophosphate ion is rapidly taken up by dental enamel, possibly by exchange of $PO_3F^{2-}$ and $PO_4^{3-}$ ions in the crystal structure, and for this reason monofluorophosphates have been suggested for the prophylaxis of dental caries.[156-7]

A study of the biochemistry and pharmacology of sodium monothiophosphate revealed that it was metabolized to hydrogen sulphide and finally to thiosulphate in the liver. Monothiophosphate can replace phosphate in the triosephosphate dehydrogenase system, but an unstable intermediate is formed. The $LD_{50}$ of sodium monothiophosphate injected intraperitoneally in mice is 950 mg./kg. body weight. In the unanæsthetized cat, intravenous injection of the substance causes depression of respiration and blood pressure. Its pharmacological effects are different from those of hydrogen sulphide.[155]

## ORGANOPHOSPHORUS COMPOUNDS

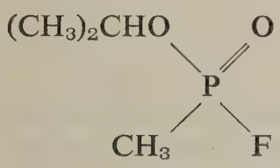
### Anticholinesterase Activity

No account of the toxicity of phosphorus compounds would be complete without some reference, however brief, to the organic derivatives of phosphorus. By far the most general and well-established type of activity is the cholinergic action shown by phosphorus esters of the structure

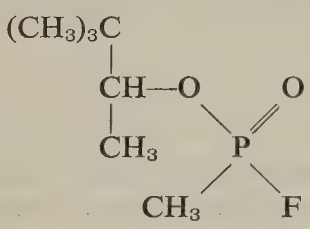


where $R_1$ and $R_2$ are alkyl, alkoxy or alkylamino groups, X is O or S, and Y is the anion of a weak acid such as cyanide, fluoride, alkyl mercaptide, p-nitrophenoxy or dialkyl phosphate.

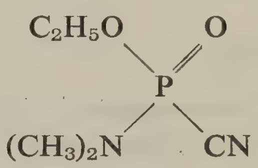
This biological activity was first observed in 1932 in diethyl phosphorofluoridates.[158] Similar compounds were subsequently developed in Germany[159] and England[160] as insecticides and chemical warfare agents. Besides a number of substances still in use as insecticides (see Table I), the German group had by 1940 developed three compounds of high mammalian toxicity, which were considered to be potential chemical warfare agents:



Sarin



Soman



Tabun

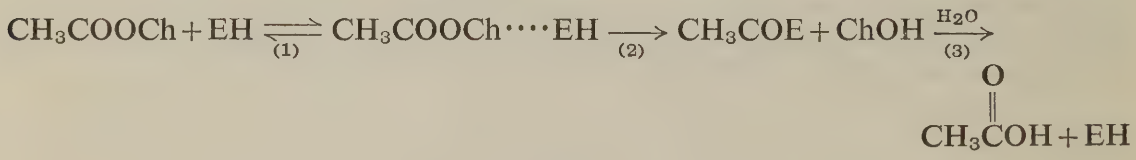
A plant capable of producing 100 tons/month of Tabun had been erected by 1945.[160] This work was reported after the war,[161-2] and led to the synthesis of a very wide variety of new compounds of similar activity.

Although the toxicity of such compounds to mammals varies widely, the symptoms of poisoning are similar. They resemble those produced by the alkaloids, eserine, muscarine and nicotine. Muscarinic effects include nausea, pallor, sweating, salivation, abdominal cramps, vomiting, involuntary defæcation and urination, miosis (constriction of the pupils of the eyes), excessive bronchial secretion and bronchoconstriction. Nicotinic effects include muscular fasciculations and weakness, leading in severe cases to muscular paralysis. There are also effects on the central nervous system, including giddiness, headache, unconsciousness and finally paralysis of the respiratory centre.[163] Death in mammals is usually caused by respiratory failure, resulting from paralysis of the respiratory muscles or the respiratory centre, or broncho-constriction.[164]

The similarity between these symptoms and those of poisoning by eserine led to the hypothesis that such organophosphorus compounds were, like eserine, potent inhibitors of the enzyme acetylcholinesterase.[165] This was later confirmed, but the inhibition was shown, unlike that by eserine, to be effectively irreversible by dilution or dialysis.[166] The cause of the inhibition was shown to be phosphorylation of the active (esteratic) centre of the enzyme.[167-8] The phosphorylated enzyme could no longer carry out its normal function of hydrolyzing the acetylcholine, which is essential for the proper action of the nervous system in the insects and higher animals. Accumulating acetylcholine then caused the symptoms described above.[169]

*In vitro* studies have shown that the reaction between the enzyme and the phosphorus compound is bimolecular ($S_N2$). It involves the attack of a nucleophilic group in the enzyme (probably an amino-acid) on the electrophilic phosphorus atom, in a manner entirely analogous to the normal enzyme-substrate reaction:

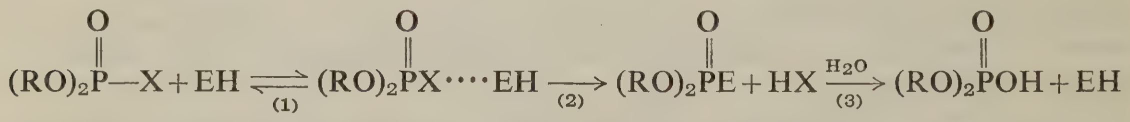
Normal reaction:



$$CH_3COOCh + EH \underset{(1)}{\rightleftharpoons} CH_3COOCh\cdots EH \xrightarrow[(2)]{} CH_3COE + ChOH \xrightarrow[(3)]{H_2O} CH_3\overset{O}{\overset{\|}{C}}OH + EH$$

$(ChOH = Me_3\overset{+}{N}CH_2CH_2OH. \qquad EH = enzyme)$

Inhibition reaction:



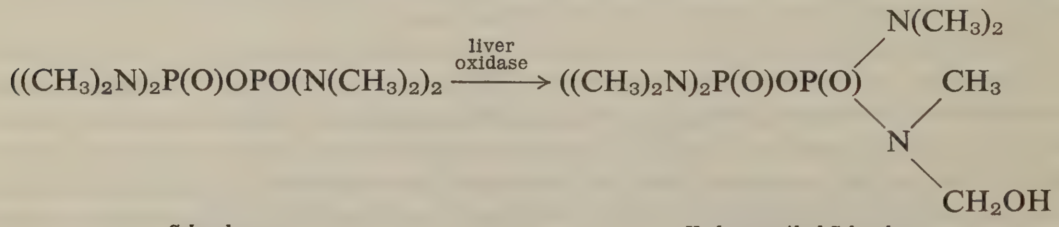
$$(RO)_2\overset{O}{\overset{\|}{P}}-X + EH \underset{(1)}{\rightleftharpoons} (RO)_2\overset{O}{\overset{\|}{P}}X\cdots EH \xrightarrow[(2)]{} (RO)_2\overset{O}{\overset{\|}{P}}E + HX \xrightarrow[(3)]{H_2O} (RO)_2\overset{O}{\overset{\|}{P}}OH + EH$$

However, in the normal reaction the hydrolysis (3) is fast and reaction (1) is rate-determining, whereas in the inhibition reaction the hydrolysis is very slow and therefore becomes the rate-determining step.[169]

The amino-acid involved in the reaction at the active site is not known for certain; histidine[170] and serine[171-2] have been suggested. There is evidence that the initial phosphorylated enzyme rearranges to another form which is more difficult to reactivate.[173]

ACTIVATION

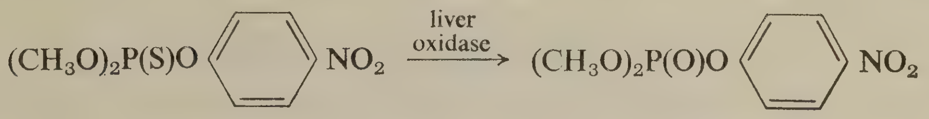
Phosphorothionates, $(RO)_2P(S)OX$, and N-methyl phosphoramidates, e.g. $Me_2NP(O)X_2$, have usually poor anticholinesterase activity *in vitro*. *In vivo* they are converted to more potent anticholinesterases by enzymes present in insects, and in the liver of mammals.[174-6] In the case of phosphoramidates such as schradan the active body is probably a hydroxymethyl compound[169]:



*Schradan*
Poor *in vitro* inhibitor

*Hydroxymethyl Schradan*
Active *in vitro*

Phosphorothionates on the other hand are metabolized to phosphates, a typical case being the formation of the potent inhibitor paraoxon from parathion:

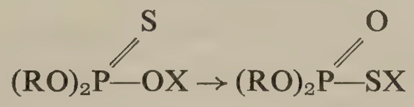


Parathion
poor inhibitor

Paraoxon
powerful inhibitor

Other reactions which can lead to an increase in anticholinesterase activity include thionate-thiolate isomerization (i) as in Systox[177];

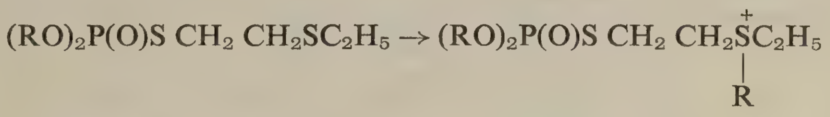
(i)



$$(RO)_2\overset{\overset{S}{/\!/}}{P}\text{—}OX \rightarrow (RO)_2\overset{\overset{O}{/\!/}}{P}\text{—}SX$$

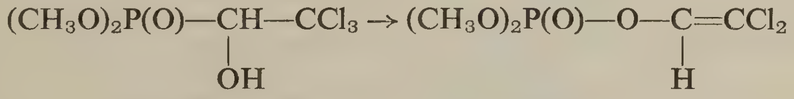
cis-trans isomerism as in Phosdrin[178]; methylation as in thiolosystox[179] (ii):

(ii)



$$(RO)_2P(O)S\,CH_2\,CH_2SC_2H_5 \rightarrow (RO)_2P(O)S\,CH_2\,CH_2\underset{\underset{R}{|}}{\overset{+}{S}}C_2H_5$$

and the unexpected dehydrohalogenation rearrangement by which Vapona (DDVP) is formed from Dipterex[180]:



$$(CH_3O)_2P(O)\text{—}\underset{\underset{OH}{|}}{CH}\text{—}CCl_3 \rightarrow (CH_3O)_2P(O)\text{—}O\text{—}\underset{\underset{H}{|}}{C}{=}CCl_2$$

Dipterex Vapona

Finally transesterification of methyl by methoxyethyl groups in methyl cellosolve solution has been shown to increase the toxicity of Dimethoate, Malathion, Ronnel, and Dow ET-15 (O-methyl O-(2,4,5-trichlorophenyl) phosphoramidothionate) several-fold.[196]

### SYNERGISM (POTENTIATION)

In certain cases mixtures of organophosphorus compounds show a higher toxicity than would be expected from a simple addition of their effects. This was first demonstrated in malathion/EPN mixtures.[181] The effect was particularly marked in dogs, where all were killed by a combination of less than 1/40 $LD_{50}$ of malathion with less than 1/50 $LD_{50}$ of EPN.[182] Tri(o-tolyl) phosphate[183] and many other substances[184] were found to have a similar effect on malathion toxicity. This was shown to be due to the inhibition of an enzyme, 'malathionase', present in the mammalian liver, which normally rapidly degrades malathion to a more harmless substance. A similar phenomenon has been observed in dipterex[195] and dimethoate.[196]

### ORGANOPHOSPHORUS INSECTICIDES

A representative selection of the commoner commercially used organophosphorus insecticides is given in Table I. The table gives the trivial name or names by which they are commonly referred to (even in the scientific literature), their systematic name, the main field of application, and the toxicity to rats by the oral route.[185-6] From what has been said above, it will be appreciated that there may be considerable variations in toxicity between batches of compound with different histories, added to the variation normally observed between animals of different sex and age, and even between different solvents used as vehicles for administration.[187] The figures given are therefore usually only an indication of the comparative order of toxicity. Other toxicity figures are given in the notes following the table. The first five compounds were the earliest to be applied commercially and have been extensively described. The remainder were developed as improvements in one way or another, and are arranged in alphabetical order of their trivial names.

*Table I.—Organophosphorus Insecticides*

| Trivial name | Systematic name | Main application* | Oral toxicity[186] to rats (LD$_{50}$) |
|---|---|---|---|
| TEPP | tetraethyl pyrophosphate | | 2(a) |
| Demeton (=Systox) | O,O-diethyl O(S)-2-ethylthioethyl phosphorothioate | SP | 2·5–12(b) |
| Dimefox (=Hanane) | N,N′-tetramethyl phosphorodiamidic fluoride | SP | 5(c) |
| Parathion | O,O-diethyl O-p-nitrophenyl phosphorothioate | BS | 6–15(d) |
| Schradan (=OMPA) | N,N′,N″,N‴-octamethyl pyrophosphoramide | SP | 14(e) |
| Co-Ral (=Coumaphos) | O,O-diethyl O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl) phosphorothioate | SA | 90–110(f) |
| Diazinon | O,O-diethyl O(-2-isopropyl-4-methyl-pyrimidyl-6) phosphorothionate | BS | 76–108(g) |
| Dimethoate | O,O-dimethyl S(-N-methylcarbamoyl-methyl) phosphorodithioate | SP | 185–245(h) |
| Dipterex (=Neguvon=Trichlorfon) | dimethyl 1-hydroxy-2-trichloroethyl phosphonate | SA | 450–500(i) |
| Disyston (=Disulfoton) | O,O-diethyl S-2-ethylthioethyl phosphorodithioate | SP | 2·5–12·5(j) |
| EPN | O-ethyl O-p-nitrophenyl phenylphosphonothioate | | 14–42(k) |
| Ethion | O,O,O′,O′-tetraethyl-S,S′-methylene-bisphosphorodithioate | | 208(l) |
| Fenthion (=Baytex) | O,O-dimethyl O-[4-(methylthio)-m-tolyl] phosphorothioate | | 190–350(m) |
| Formothion | O,O-dimethyl (N-methyl-N-formyl-carbamoylmethyl) phosphorodithioate | | —(n) |
| Guthion (=Azinphosmethyl) | O,O-dimethyl S-(4-oxo-1,2,3-benzotriazin-3(4H)-yl-methyl) phosphorodithioate | BS | 7–17(o) |
| Malathion | O,O-dimethy S-(1,2-dicarboethoxy-ethyl) phosphorodithioate | BS | 2800(p) |
| Metasystox (=Methyl demeton) | O,O-dimethyl S-(2-ethylthioethyl) phosphorothiolate | SP | 65–75(q) |
| Methyl Parathion | O,O-dimethyl O-p-nitrophenyl phosphorothionate | | 9·4(r) |
| Phorate (=Thimet) | O,O-diethyl S-(ethylthiomethyl) phosphorodithioate | SP | 1·6–3·7(s) |
| Phosdrin (=Mevinphos) | O,O-dimethyl O-(2-carbomethoxy-1-methylvinyl) phosphate | SP | 6–7(t) |
| Ronnel (=Trolene=Dow ET–57) | O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate | SA | 1,750(u) |
| Ruelene | O-(4-tert.butyl-2-chlorophenyl) O-methyl N-methylphosphoramidate | SA | 660–1,000(v) |
| Sumithion | O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothionate | BS | 250(w) |
| Vapona (=DDVP=Dichlorvos) | O,O-dimethyl O-(2,2-dichlorovinyl) phosphate | | 56–80(x) |

* SP=Systemic in plants; SA=Systemic in animals; BS=Broad spectrum (general application).

(a) Other values (LD$_{50}$ mg./kg.): Mouse, or. 7·0, s.c. 0·9–1·0, i.p. 0·85; rat, or. 1·2–2·0, s.c. 0·7, inh. 0·8–1·0; guinea-pig, or. 2·3; rabbit, ct. 2·0–5. Estimated lethal dose in man 100 mg. oral.[198]

(b) Other values (LD$_{50}$ mg./kg.): Rat, or. 1·5 (thiol), 7·5 (thiono), 9·4, ~9, 10, 4, i.p. 3; rabbit, ct. 24; man estimated acute dose 10–20 mg.[198]; rat, or. 6·4–7·9, i.p. 4·6.[194]

(c) Other values ($LD_{50}$ mg./kg.): Rat, or. 7·5, i.p. 5·0; mouse 1·0 s.c., 1·4–5·0 i.p.; guinea-pig, i.p. 2·5[198]; for a review see ref. 201.

(d) Other values ($LD_{50}$ mg./kg.): Rat, or. 6·4–16·9, i.p. 4·6–14·4, i.v. 1·05–5·4, s.c. 7·8–13·6[187]: Rat, or. 3·0–30·0 (10 determinations), i.p. 4–7, i.v. 3; guinea-pig, or. 32; rabbit, ct. 40–50, 420, 870; cat, i.p. 3–5; dog, i.p. 12–20. Man, estimated lethal dose 20–100 mg. The chronic toxicity of parathion is fairly low, though repeated exposure increases the susceptibility to larger doses. Several deaths reported due to careless use including one from 120 mg. taken orally.[198]

(e) Other values ($LD_{50}$ mg./kg.): Mouse, or. 30, s.c. 1·5–7, i.p. 8–17; rat, or. 10–35·5 (4 determinations), i.p. 8–8·5; guinea-pig, or. 15·0, i.p. 10·0; rabbit, or. 25, ct. < 780; dog, i.v. 5–10. The upper safe therapeutic dose for man, in the treatment of myasthenia gravis is 30 mg./day.[198]

(f) Other values ($LD_{50}$ mg./kg.): Rat, or. 56–230.[185] For an account of Co-Ral poisoning in cattle see ref. 202.

(g) Other values ($LD_{50}$ mg./kg.): Mouse, or. 82, 100, 122·5; rat, or. 100–150, 264·5, 220–270, 712·5, 900; guinea-pig, or. 320 mm.$^3$/kg.; rabbit, ct. > 4,000[198]; rat, or. 293–408, ct. > 1,000.[188]

(h) Other values ($LD_{50}$ mg./kg.): Rat, or. 247, ct. 1120.[188] For synergism with other substances see ref. 196.

(i) Other values ($LD_{50}$ mg./kg.): Rat, or. 450–500, i.p. 225; mouse, or. 500; guinea-pig, or. 300[198]: rat, or. 649, ct. > 2,800[188]; calves, or. > 220[189]; sheep, or. > 165[190] (see also ref. 191 and (for synergism with other insecticides)).[195]

(j) Other values ($LD_{50}$ mg./kg.): Rat, or. 2–12·5.[185] For a review of toxicity and mechanism of action, see ref. 204.

(k) Other values ($LD_{50}$ mg./kg.): Mouse, or. 45·5, i.p. 48; rat, or. (24 hr.) 12–76: or. 7–91, i.p. 24, 64; guinea-pig, or. 79·4. The variability of toxicity, between sexes and between species, is high. Many further data are given in the reference 198.

(l) Other values ($LD_{50}$ mg./kg.): Rat, or. 96; rabbit, ct. 915[185].

(m) Rat, or. 325 mg./kg.[185] (see also ref. 192).

(n) Rat, or. 35 mg./kg.[193]

(o) Other values ($LD_{50}$ mg./kg.): Rat, or. 12, ct. 220.[185]

(p) Other values ($LD_{50}$ mg./kg.): Mouse, or. 720–3300 (6 values); rat, or. 300–4700 (10 values), ct. > 4,000, i.p. 750, i.v. ~ 50; guinea-pig, or. 570[198]: rat, ct. > 5,000, or. 1,375[185]: rat, or. 233–1400, i.p. 132–695, i.v. 184–453[187]: mouse, or. 815.[194]

(q) Other values ($LD_{50}$ mg./kg.): Rat, or. 80[185]: rat, or. 129, ct. 443[188]: rat, or. 63, i.v. 65.[179] For the toxicity of the sulphoxide (Metasystox R) see ref. 205.

(r) Other values ($LD_{50}$ mg./kg.): Rat, or. 9–25, 15·2, 14–42, i.p. 3·5; mouse, or. 100–200, s.c. 50–100; rabbit, or. 420–1270[198]; rat, or. 17·1–58, i.v. 2·3–14·2, i.p. 8·6–18·5, s.c. 18·0.[187]

(s) $LD_{50}$ or. rat 3·7 mg./kg.[185]

(t) $LD_{50}$ or. rat 6·8 mg./kg.[185]

(u) Effective dose 100 mg./kg.[185] (see also ref. 197).

(v) $LD_{50}$ or. rat 1,000 mg./kg.[185]

(w) Other values ($LD_{50}$ mg./kg.): Mouse ct. > 3,000[185]: rat, or. 673, ct. > 3,000; mouse, or. 870, ct. > 3,000; guinea-pig, or. 1,833.[199]

(x) Other values ($LD_{50}$ mg./kg.): Rat, or. 80[185]: rat, or. 56–80, ct. 75–107.[198, 200]

It will be seen from Table I that there is a wide variation in the mammalian toxicity of the organophosphorus anticholinesterase insecticides. While the first to be discovered were quite toxic to mammals, some more recent examples have oral toxicities one or two orders lower. However, the toxicity to insects does not always parallel that to mammals: indeed it has been pointed out that these compounds can be divided into three classes, according to whether their mammalian toxicity is much greater than, roughly equal to, or much less than, their toxicity to insects.[169, 203]

It is obvious that while members of the first class are highly hazardous in use, the third class of ‘selective insecticides’ can be used with relative safety. Thus such compounds as Ronnel, Ruelene or Co-Ral can be safely given to animals in doses high enough to make their tissues toxic to parasites such as cattle flies, lice, mites, ticks, screw-worm larvæ or helminths.[189] This parallels the action of systemic plant insecticides such as Demeton or Schradan which have been known much longer.[185]

Members of the first class of ‘selective mammalicides’, on the other hand, have been proposed as war gases. They are toxic both by inhalation and by absorption through the skin.[213] The most toxic of those commonly reported is Sarin (*iso*propyl methylphosphonofluoridate ($LD_{50}$ (mg./kg.) 0·127 s.c. (rats),[215] 0·036 inhalation (dogs)[216]). Symptoms of poisoning in man are typically muscarinic and nicotinic, as described above.[217] Tabun (ethyl N-dimethyl phosphoramidocyanidate) is somewhat less toxic ($LD_{50}$ ~ 0·8 mg./kg. s.c. (rats)).[213–4] Other compounds proposed for the same purpose include di-*iso*propyl phosphorofluoridate (DFP), $LD_{50}$ (mg./kg.) 36·8 oral, 3·71 s.c. (mice): 1·82 i.v. (rats): 9·78 oral, 0·34 i.v. (rabbits):

*Table II.—Selective Toxicity of Some Organophosphates*[(a)]

| Compound | Mammal used | Housefly treatment: injected (i) or topical (t) | $LD_{50}$ mammal/ $LD_{50}$ housefly |
|---|---|---|---|
| Selective insecticides | | | |
| Malathion | Mouse | t | 68 |
| Dimethoate | Mouse | t | 325 |
| Co-Ral | Mouse | t | 16 |
| Diazinon | Mouse | t | 27 |
| Dipterex | Rat | t | 31 |
| Selective mammalicides | | | |
| Schradan | Rat | t | 0·009 |
| Iso-Systox methosulphate | Mouse | i | 0·03 |
| Tetram | Mouse | i | 0·00042 |
| Ro 30412 | Mouse | i | 0·004 |
| Nonselective compounds | | | |
| Phosdrin isomers | Rat | t | 0·8 |
| Parathion | Mouse | t | 6 |
| DFP | Rat | t | 9 |
| Thimet | Rat | t | 6 |
| TEPP | Mouse | t | 0·17 |

(a) $LD_{50}$'s at 24 hr. Mouse: intraperitoneal application. Rat: subcutaneous application.

3·43 i.v. (dogs): 1·63 i.v. (cats)[218] and N,N′-tetramethylphosphorodiamidic fluoride, $LD_{50}$ 1 mg./kg. s.c. (mice). An estimate of the toxicity to man of these substances, compared with that of better known war gases, has been published,[219] see Table III.

*Table III.—Comparison of Toxicity of Nerve Gases and Other Agents*

| Agent | Median lethal breathing[(a)] dose (mg. min. $m^3$) | Lethal dose percutaneous[(b)] (mg.) |
|---|---|---|
| Tabun | 100–200 | 200–400 |
| Sarin | 50–100 | 100–200 |
| DFP | 1500–2000 | — |
| Phosgene | 3300 | — |
| Mustard gas | 1500 | 4000–5000 |

(a) Median lethal dose is the dose which would be expected to kill 50 per cent of the population subjected to it.
(b) Estimated for man, published Swedish figures.

Further details of the toxicology and pharmacology of these substances are given in a number of reviews.[159–60, 169, 198, 220–2, 230] Of particular interest is the review by Schrader[223] of the relation between structure and activity.

### THERAPY OF ORGANOPHOSPHATE POISONING

Poisoning by phosphorus anticholinesterases was first treated by injection of atropine, which counters their muscarinic action[12] but has undesirable effects of its own. More recently it has been found that nucleophilic agents such as hydroxylamine,[206] hydroxamic acids,[207] *iso*nitroso compounds,[208] and oximes, especially pyridine-2-aldoxime methiodide (2.PAM),[209–10] will reactivate freshly inhibited cholinesterase. The latter compound, and the corresponding methanesulphonate, have been used with success in treating a number of cases of human poisoning, particularly by parathion.[211] Instructions for the treatment of patients suffering from poisoning by organophosphorus anticholinesterases have been issued.[212]

### Demyelinating Action

A number of organophosphorus compounds can produce in man a characteristic multiple neuritis, which in severe cases can lead to a flaccid paralysis. The condition was first observed clinically in 1930 in the United States, when about 20,000 people were affected after drinking a contaminated alcoholic extract of ginger ('ginger jake'). The effects were soon shown to be due to tri-ortho-cresyl phosphate (TOCP) which was present in the extract to the extent of 2%.[224] Aryl phosphates made from phenolic mixtures containing *o*-cresol have been extensively used since then, as plasticizers, functional fluids, and petrol and lubricating-oil additives, and many more cases of poisoning have been reported, some leading to death or permanent paralysis.[12, 225] The major disasters have always been associated with the adulteration of food or drink. Thus in an outbreak of poisoning in Morocco in 1959, 10,000 persons were affected by cooking oil adulterated with jet-engine lubricating-oil containing 3% mixed cresyl phosphates.[227] The clinical picture presented in such cases is always similar. After transient gastro-intestinal disturbances there is a latent period of 1–4 weeks, after which the characteristic symptoms of flaccid paralysis of the feet and wrists appear, preceded by soreness or pains in the affected muscles. The feet and legs are always more affected than the hands and fore-arms and the upper arms and the large muscles of the thigh are seldom affected. There is no sensory disturbance[225] and no involvement of the cranial nerves. Mildly affected patients can recover completely,[169] but in severe cases paralysis may be permanent.[226]

The lesions which cause paralysis consist in the degeneration of the myelin sheath of the peripheral nerves, the white matter of the spinal cord, and of the pyramidal cells.[169, 12] Experimental studies have shown that humans, calves and chickens over 4 months old are paralysed by TOCP given by any route. Dogs and monkeys are unaffected by large doses given orally, but develop the characteristic symptoms after subcutaneous or intramuscular dosage.[224] Rats seem to be little affected by TOCP, however administered.[228] Young chicks are also insensitive to TOCP poisoning.[229] The minimum paralytic dose in man has been estimated to be between 10 and 30 mg./kg.[230]

Intravenous injection of TOCP in cats caused typical symptoms. The effects were cumulative, the minimum lethal dose for cats being about 0·1 ml./kg. whether given at one time or over a period. Larger doses tended to cause more rapid and severe paralysis.[231]

Although tri-*o*-cresyl phosphate was the first compound implicated in this way it was soon found that other aryl phosphates behaved similarly, although only the tri-esters were toxic. Thus mono-*o*-cresyl dihydrogen phosphate gave only transient symptoms of cresol poisoning and di-*o*-cresyl monohydrogen phosphate produced no effects on the nervous system.[232]

Of triaryl phosphates, triphenyl phosphate produced an atypical generalized delayed paralysis in cats and monkeys, but appeared to be without effect in man, chickens or rabbits.[233] Aryl phosphates made from mixed alkyl phenols caused paralysis, however, those containing only one *o*-cresyl group being the most highly toxic. The toxicity of *o*-cresyl diphenyl phosphate was found to be twice that of *o*-cresyl *m*-cresyl *p*-cresyl phosphate, 20 times that of tri-*o*-cresyl phosphate, and 80 times that of *o*-cresyl di-(3,5-xylyl) phosphate.[234–5] This work was later confirmed and extended.[236–7] No universal rule connecting toxicity with structure could be established, though certain regularities appeared. Thus from Table IV it will be seen that compounds containing one, two or three 2-Me phenyl groups are toxic, other groups exerting a modifying effect on the toxicity (e.g., 2Me 4Me 4Me > 2Me 3,5diMe 3,5diMe). The 2-Me group must be the sole substituent in the ring, since tris-2,3, tris-2,5 and tris-2,6 diMe-phenyl phosphates are not toxic.[237]

No similar generalizations are possible for ethyl or propyl substitution: e.g., tris-2-Et- and tris-2-Pr-phenyl phosphates are non-toxic, 2-Pr-phenyl bis-4-Et-phenyl phosphate is very toxic, 2-Pr-phenyl bis-3,5-diMe phenyl phosphate is again non-toxic. Finally tris-4-ethylphenyl phosphate is unexpectedly toxic,[239] whereas all other 4-alkyl substituted derivatives (including tris-2-Me-4-Et-phenyl phosphate) are not.[237]

Many of the compounds inhibited plasma or brain pseudo-cholinesterase and liver or intestinal phenylbutyrate esterase, but again there was no correlation between these activities and neurotoxicity.[237]

*Table IV.—Neurotoxic Activity of Tris-(alkylphenyl) Phosphates*[236–7]

(The position of substitution in the three phenyl radicals is indicated by arabic numerals, followed by an abbreviation showing the nature of the substituent alkyl groups.)

| Very toxic(a) | Toxic(b) | Slightly toxic(c) | Non-toxic(d) |
|---|---|---|---|
| 2Me 4Me 4Me | 2Me 2Me 2Me | 2Me 2Me 4Me | 3Me 3Me 3Me |
| | 2Me 2Me 3Me | 2Me 3,5diMe 3,5diMe | 4Me 4Me 4Me |
| 2Et 4Me 4Me | 2Et 2Et 4Me | 2Et 3,5diMe 3,5diMe | 2Et 2Et 2Et |
| | 4Et 4Et 4Et | | 3Et 3Et 3Et |
| | | | 3Et 3Et 4Et |
| | | | 3Et 3Et 4Me |
| | | | 4Et 4Et 4Me |
| | | | 4Et 4Me 4Me |
| | | | 4Et 3,5diMe 3,5diMe |
| 2Pr 4Et 4Et | | 2Pr 2Pr 4Me | 2Pr 2Pr 2Pr |
| | | | 2Pr 3,5diMe 3,5diMe |
| | | | 2Cl 2Cl 2Cl |
| | | | tri-(2Me 4Et) |

(a) Caused ataxia in a single dose of < 100 mg./kg.
(b) Caused ataxia in a single dose of 200–500 mg./kg.
(c) Caused ataxia in single or successive doses totalling > 1000 mg./kg.
(d) Caused no ataxia at doses up to 5 × 500 mg./kg.

Further search has revealed similar neurotoxic activity in other organophosphorus compounds.[229, 238, 241] Severe paralysis in two workers exposed to the insecticide Mipafox (N,N′ di-*iso*-propyl phosphorodiamidic fluoride)[240] led to the discovery that this substance was capable of causing nerve demyelination in hens.[229] Other workers showed that phosphorofluoridates (e.g., DFP) and phosphonofluoridates (e.g., Sarin) has a similar effect. Dialkylphosphinic fluorides, dialkyl pyrophosphonates, and other alkyl phosphate esters not containing fluorine, were not toxic. In general compounds of the formula (RA)R′P(:B)F were found to be neurotoxic if R was an alkyl group, R′ alkyl alkoxyl or alkylamino group, A was O or a secondary amine group, and B was O or S.[241] Trimethyl phosphate[242] and aryl phosphites[243] have also been reported to cause paralysis in certain mammals, though no cases in man are known.

### MISCELLANEOUS ACTIVITY

In general alkyl phosphates are not very toxic, though tris-2-chloroethyl phosphate produces epileptiform convulsions in the rat at a level of 0·28 g./kg. (i.p.). Toxicological data have been recorded for a range of phosphates,[230] median lethal doses being in general around 1 g./kg. Alkyl phosphites are of a similar order of toxicity.[230] A single study of trimethyl and triethyl trithiophosphites, however, showed these to be highly toxic to rats ($LD_{50}$ (i.p.) 44 mg./kg. or 105 mg./kg. for the trimethyl compound). Death was due to circulatory collapse.[244]

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# INDEX

*Introductory note.* The diversity of constitution of phosphorus compounds and their complex nomenclature have made indexing difficult in some instances. The following points may help the user of the index:

1. If a specific compound is not found in the Index, refer to the parent *group*; in covering organophosphorus compounds, particularly, it has not been feasible to list every individual compound treated under a group heading. Salts of acids or bases are usually treated under the parent acid or base. (Note that in Mellor, phosphates are treated in volumes covering the metallic components; phosphides, however, are considered in detail in this volume and indexed under their metal constituents.)

2. 'Phosphoric oxide' is indexed under 'Phosphorus pentoxide', and the suffixes '-ic' and '-ous' are avoided in indexing binary compounds. Halides are listed as 'trichloride', 'pentachloride', etc. Mixed halides are distinguished by formula under headings such as 'Phosphorus trihalides'. For clarity, certain compounds not quickly recognizable by name are also quoted by formula under appropriate general headings.

3. The prefixes 'ortho-', 'meta-', and 'pyro-', used particularly in regard to the phosphoric acids, are regarded as separable, and 'orthophosphoric acid' is indexed under 'Phosphoric acid, ortho-'; similarly in other cases. Variety of modes of use prohibits any general rule for the use of 'mono-', 'di-', 'tri-', 'tetra-', 'poly-', 'iso-', 'hypo-', etc., and in any case of difficulty the appropriate alternatives should be tried in referring to the index; for example, 'Hypophosphites' might have been indexed as 'Phosphites, hypo-', and 'Chlorophosphoric acid, di-' might have been referred to as 'Dichlorophosphoric acid'. In instances of this kind, the alternative chosen has often been determined by a need to put analogous compounds in close proximity in the index.

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